

Resonance Effect on the Moderation of Slow Electrons in Diatomic Gases

J. A. STEPHENS AND F. ROBICHEAUX

The James Franck Institute, The University of Chicago, Chicago, Illinois 60637

STEPHENS, J. A. AND ROBICHEAUX, F. Resonance Effect on the Moderation of Slow Electrons in Diatomic Gases. *Radiat. Res.* 110, 19-34 (1987).

A survey of stopping power, range, moderation rate, and moderation time for slow electrons in pure gases of H₂, N₂, CO, and O₂ is reported. By employing experimental and theoretical cross-section data, contributions to these quantities from vibrational excitation, rotational excitation and deexcitation, and elastic energy transfers are included. The influence of low-energy molecular shape resonances and their effect on electron degradation processes is discussed and emphasized. © 1987 Academic Press, Inc.

I. INTRODUCTION

The action of ionizing radiations in gaseous or condensed media can give rise to a substantial population of secondary, low-energy electrons. These "subexcitation" electrons actually deliver a substantial fraction of the total energy imparted by the ionizing radiations (*I*). This paper studies the moderation of subexcitation electrons in diatomic gases by examining their stopping power, and other derived slowing-down quantities.

In collisions of fast electrons with molecules the cross section for excitation to various accessible states (and thus the stopping power, defined by Eq. (1) below) separates into a quantity depending on the incident electron only and a molecular property known as the generalized form factor (2, 3). For slow collisions, on the other hand, the electron and material properties cannot be simply separated. The dynamics of these collisions often involve the formation of a temporary negative-ion complex, which enhances energy transfer to the nuclear motion and thereby contributes heavily to the electron degradation.

The stopping power of a molecular gas for slow electrons is accordingly assembled from elementary collision cross sections, obtained from experiment and theory, through the definition (3)

$$-\frac{dT}{dx} = N \sum_i p_i \sum_n E_{ni} \sigma_{ni}(T). \quad (1)$$

Here N is the molecular number density, p_i is the fraction of molecules in state i , $\sigma_{ni}(T)$ is the cross section for excitation from state i to n at incident electron kinetic energy T , and $E_{ni} = E_n - E_i$ is the energy transfer, E_n and E_i being the eigenenergies of the states involved. Equation (1) can effectively be evaluated directly in the subexci-

tation domain by taking into account energy losses due to quasielastic collisions, rotational excitation and deexcitation, and vibrational excitation (4-6). Inokuti *et al.* (4) and Takayanagi (6) have discussed the relative importance of each of these energy loss modes. For example, even though the energy loss from elastic collisions is extremely small (of order $2m/M$, where m is the electron mass and M is the molecular mass) the elastic cross section is very *large* and may make appreciable contribution to Eq. (1). It is generally observed that the vibrational contribution dominates the slowing down of the subexcitation electrons, especially in the vicinity of negative-ion resonances. However, since these resonances are quite localized in energy, the elastic and rotational losses become important outside this region and are required for proper description of the moderation.

The aim of the present study is threefold. First, we systematically survey and discuss the important effect that *resonances* have on the slowing down of electrons in the subexcitation domain. The mechanism of formation and physical properties of these resonances in molecules have been discussed and reviewed by Schulz (7) and more recently by Lane (8), Csanak *et al.* (9), Trajmar and Cartwright (10), and Hasted and Mathur (11). In this paper, we are primarily concerned with the effect of *shape resonances* on the moderation of slow electrons, since these are most relevant to the subexcitation domain. Dehmer (12) has recently given a discussion of the dynamics of molecular shape resonances. Specifically we examine slow electron moderation in pure gases consisting of molecular hydrogen, nitrogen, carbon monoxide, and oxygen. This choice reflects both the interest in studying the moderation for target molecules of increasingly complex electronic structure and also the availability of reliable experimental and theoretical collision data. The differing complexity of electronic structure implies important differences in the dynamics of formation and decay of the shape resonances, e.g., the lifetime, resonance position, and *relative* positions of resonant structures within alternative vibrational decay modes. The latter point has important consequences for the appearance of discrete structure in the stopping power and slowing-down properties and is discussed below for the specific example of oxygen.

Second, the effects of shape resonances on the moderation of slow electrons in gases are quite relevant to their moderation in condensed phases. Sanche and Michaud (13) have observed and interpreted resonances in the condensed phases of N_2 , CO, and O_2 , which were shown to be essentially identical to the $^2\Pi$ configurations of the shape resonances of the free molecules. Moderation processes for slow electrons in the condensed phase depend explicitly on the rovibronic structure of individual molecules, and the contribution to degradation from these resonances is substantial. In spite of this situation, there is yet no theoretical formulation of slow electron degradation in condensed systems comparable to that of fast electrons and other ionizing radiations (14, 15). Fano and Stephens (16) have recently discussed and introduced relevant concepts to treat energy loss and distribution of subexcitation electrons in condensed matter.

Finally, since the slowing down properties should be of significant interest to radiation chemists or biologists for use in further calculations (e.g., yields of excited molecular species and mean terminal times), all results will be made available, upon request, in tabulated form. In the calculation of the stopping power, we have attempted

to use the most reliable and recent cross-section data available. We have also obtained estimates of the electron range and moderation time, within the continuous-slowing-down approximation (CSDA), by simple integration of the stopping power and moderation rate. Investigation of the validity of the CSDA (especially in the vicinity of shape resonances and associated vibrational structure in the stopping power) is beyond the scope of the present paper but nonetheless merits further study.

The remainder of this paper is organized as follows. Section II discusses the methods and the experimental and theoretical data used to evaluate the slowing down quantities. Section III compares and discusses the stopping power for the four molecules. Section IV discusses and compares the various moderation quantities, i.e., the moderation rate, moderation time, and range. Section V gives a brief summary and conclusion.

II. CALCULATION

The calculation of electron stopping power is straightforward when complete sets of absolute cross sections have been assembled for all relevant energy loss processes over the kinetic energy range of interest. In addition to the stopping power (defined by Eq. (1)) three useful moderation parameters are derived in terms of the stopping power:

Moderation rate. The mean rate of energy loss of an electron of energy T is

$$-\frac{dT}{dt} = -\frac{dT}{dx} v(T), \quad (2)$$

where $v(T)$ is the electron's velocity.

Moderation time. The mean time required for an electron to degrade from T_i to T is

$$\mu(T, T_i) = \int_T^{T_i} dT' \left(-\frac{dT'}{dt} \right)^{-1}, \quad (3)$$

where T_i is the initial kinetic energy.

Range. The mean distance traveled by an electron as it degrades from T_i to T is

$$R(T, T_i) = \int_T^{T_i} dT' \left(-\frac{dT'}{dx} \right)^{-1}. \quad (4)$$

Equations (3) and (4) are valid in the continuous-slowing-down approximation, the usual criterion for its validity being that the energy loss be a small fraction of the electron's kinetic energy. Douthat (17, 18) has further discussed the validity of the CSDA in the subexcitation domain.

We evaluated Eqs. (1)–(4) for the H_2 , N_2 , CO , and O_2 molecules for the kinetic energy range $T_i = 8.0$ eV to $T_f = 0.054$ eV for a gas temperature of 23°C . In addition to Eq. (1), the stopping power due to elastic collisions was calculated from the formula (19)

$$S_{\text{elastic}}(T) = \frac{2m}{M} T \sigma_{\text{mt}}(T), \quad (5)$$

TABLE I
Sources of Electron Scattering Cross-Section Data

<i>Molecule</i>	<i>Momentum transfer</i>	<i>Rotational</i>	<i>Vibrational</i>
H ₂	20, 21	20, 22	22, 23
N ₂	24, 25	26, 27	28-31
CO	32	33	23, 34
O ₂ ^a	35, 36	37	38

^a Excitation cross sections for the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states of O₂ were obtained from Refs. (38) and (39).

where $\sigma_{mt}(T)$ is the momentum-transfer cross section. The kinetic energy range was chosen mainly to encompass the subexcitation domain of all the molecules and to emphasize the importance of resonance effects in the slowing-down quantities.

Table I summarizes the experimental and theoretical data sources from which cross sections were employed in calculation of the stopping power. Many of the experimental references and cross-section data have been compiled in a review article by Trajmar *et al.* (40). We have considered literature since that review and have consulted all original articles in selecting data for the calculations. Except for H₂, complete sets of rotational excitation and deexcitation cross sections were obtained from theoretical data. To obtain the large sets of rotational excitation cross sections which are required for calculating the stopping power at room temperature, the adiabatic approximation was used to appropriately scale a given "basic" cross section, such as the $0 \rightarrow 2$ excitation in H₂. In the rotational adiabatic approximation (37, 41), the cross section $\sigma_{j' \rightarrow j}$ depends *analytically* on the rotational quantum numbers j and j' , and the angular momentum transfer $j_t = j' - j$ through combinations of the Wigner coefficient $(j0j'0|j_t0)^2$. The microscopic reversibility relation $(2j' + 1)\sigma_{j' \rightarrow j} = (2j + 1)\sigma_{j \rightarrow j'}$ was then used to obtain complete sets of rotational deexcitation cross sections.

All molecular constants used in calculating the energy loss for the vibrational and rotational modes were obtained from the compilation of Huber and Herzberg (42). We briefly discuss specific considerations in the data selections for each molecule.

Douthat (17) has previously reported a set of stopping cross sections for H₂ which were used in a full treatment of electron degradation by solving the Spencer-Fano equation for the track length spectrum. We have extended the Douthat compilation by including energy loss to the $v = 2, 3$ vibrational levels (23) in addition to rovibrational energy losses corresponding to the excitations $v = 0, j = 0, 2, 3, 4 \rightarrow v = 1, j = 2, 4, 5, 6$. We also included energy losses due to pure rotational deexcitation. Allen (43) recently has measured vibrational excitation to the $v = 4-6$ levels, but these give negligible contribution to the stopping power. Inclusion of these additional processes increased the total stopping power by $\sim 11\%$ over the Douthat values in the range 2-8 eV kinetic energy. H₂ is the only molecule with measured rovibrational cross sections, and therefore a choice must be made in using these data, the unresolved $v = 0 \rightarrow 1$ data of Ehrhardt *et al.* (23), or the recent measurement of Nishimura

et al. (44).¹ Calculations of the total stopping power using the resolved Linder and Schmidt (22) cross sections, including scaling, and the unresolved data of Ref. (23) give nearly identical results. We believe that using the rovibrational cross sections in this case give slightly more accurate results.²

For N₂, the reported vibrational cross sections up to ~3 eV are in arbitrary units, so that a normalization must be chosen. We employed the recent absolute measurement of the $v = 0 \rightarrow 1$ cross section at 2.25 eV by Jung *et al.* (29). This value is in excellent agreement with the accurate R-matrix calculations of Schneider *et al.* (45), and the scaled results of Schulz (28) joined smoothly with the absolute cross sections of Tanaka *et al.* (30) in the 3–8 eV range. The $v = 2$ results of Schulz (28) were extended from 3.5 to 4 eV kinetic energy using the measurements of Ehrhardt and Willman (31).

For CO, there is discrepancy in the literature concerning the absolute normalization of the vibrational excitation cross sections.³ We have employed the cross sections of Ehrhardt *et al.* (23) and have extended their $v = 0 \rightarrow 1$ cross section to 8 eV kinetic energy using the 5 and 9 eV data of Chutjian and Tanaka (34). The data of the latter authors at 3 eV had to be increased by a factor of 1.8 to be made consistent with those of Ref. (23). We chose the absolute normalization of Ref. (23) because the sum of these inelastic cross sections in the resonance region (at 2 eV kinetic energy) and a reliable theoretical value (33) of the elastic cross section is in good agreement with the total cross section reported by Szymkowski and Zubek (46). The sum of these vibrational cross sections at 2 eV is also in good agreement with the value reported by Schulz (28).

To meaningfully compare the O₂ stopping power with the other molecules over a range extending to 8 eV kinetic energy, we have also included electronic excitation to the O₂ $a^1\Delta_g$ and the $b^1\Sigma_g^+$ valence states. The subexcitation range is strictly defined only for kinetic energies below the first electronic excitation threshold of the molecule. For the molecules H₂, N₂, CO, and O₂, these thresholds, respectively, are 11.4, 6.2, 6.0, and 0.98 eV (42).

III. RESONANCES IN THE TOTAL STOPPING POWER

In Fig. 1 we show plots of the total stopping power $-dT/dx$ for each of the four molecular gases. This plot emphasizes the striking differences in structure and magni-

¹ The $v = 0 \rightarrow 1$ cross sections of Refs. (23) and (44) agree within their experimental error bars. The $v = 0 \rightarrow 1$ cross section calculated from the data of Ref. (22) according to $\sigma(v = 0 \rightarrow 1) = \sigma(v = 0 \rightarrow 1, \Delta j = 0) + 1.12\sigma(v = 0 \rightarrow 1, j = 1 \rightarrow 3)$ also agrees within the experimental error bars of these sources. The factor 1.12 represents contributions from relevant $v = 0, j = 0-4$ initial states. See Ref. (22).

² By analysis of the "unresolved" vibrational stopping cross section $(E_{v'} - E_v)\sigma(v \rightarrow v')$ and the exact rovibrational stopping cross section $\sum_{j,j'} (E_{v'j'} - E_{vj})p(j)\sigma(v \rightarrow v', j \rightarrow j')$, we find implicit error terms of order $(E_{j'} - E_j)p(j)\sigma(v \rightarrow v', j \rightarrow j')$ in the unresolved case. E_{vj} are the rovibrational energy levels and $p(j)$ is the fraction of molecules in rotational state j . At an electron kinetic energy of 3 eV, we calculate these terms to be ~2% of the total stopping power in the case of H₂.

³ This discrepancy has been discussed in some detail by Chutjian and Tanaka (34). The vibrational cross sections reported in Refs. (23), (32), and (34), respectively, differ from each other by a factor of two or greater.

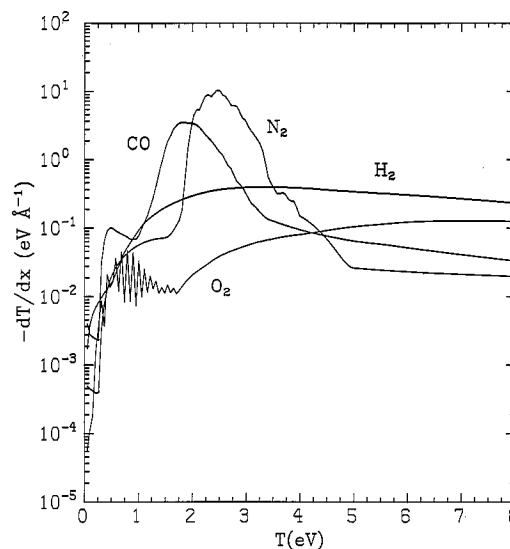


FIG. 1. Total electron stopping power for H_2 , N_2 , CO , and O_2 . These curves, and those for all remaining figures, are normalized to unit number density ($N = 1 \text{ Å}^{-3}$ in Eq. (1)).

tude of the stopping power of each material within the subexcitation domain. The extreme variations of the stopping power of these molecules result from the relative importance of the short- and long-range electron-molecule interactions in the subexcitation energy range. The peaks due to the shape resonances (which derive from short-range interactions) are the most conspicuous features (7) and result from the sum effect of the resonances present in *each* constituent cross section. For convenience and purpose of discussion, we list in Table II relevant properties of the shape resonances which are prominent in the stopping powers in Fig. 1. The lifetimes and symmetries have been compiled from the data sources used for the stopping power calculations. Christophorou (47) has reviewed and surveyed the lifetimes of the temporary negative-ion states in these and many polyatomic molecules as well. The behavior of the stopping power and moderation parameters outside the shape resonance region (which reflect mainly long-range interactions) is discussed in the next section.

TABLE II

Summary of Shape Resonance Parameters

Molecule	E_r^a (eV)	Lifetime (s)	Symmetry ^b	Partial wave
H_2	3.34	$\sim 10^{-15} - 10^{-16}$	$2\Sigma_u^+$	$p\sigma_u$
N_2	2.45	$\sim 1.4 \times 10^{-15}$	$2\Pi_g$	$d\pi_g$
CO	1.87	$\sim 1.1 \times 10^{-15}$	2Π	$p\pi, d\pi$
O_2	0.69	$\sim 10^{-10} - 10^{-12}$	$2\Pi_g$	$d\pi_g$

^a E_r is the resonance energy of the principal peak in calculated stopping power.

^b Symmetry is for $e^- + \text{molecule complex}$.

The molecules H_2 and O_2 represent two extreme cases of shape resonance lifetime (width). Since the lifetime of the H_2 $^2\Sigma_u^+$ shape resonance near 3 eV is much shorter than one vibrational period, there can be only very weak vibrational excitation. Similarly the short resonance lifetime appears to prevent the formation of vibrational substructure in the cross sections or stopping power. Remarkably, Allen (43) has recently observed vibrational substructure in the $v = 3-6$ excitation functions of H_2 , but due to the small magnitude of the cross section, their effect on the stopping power is negligible. On the other hand, the long lifetime of the O_2^- negative ion has significant implications for the structure and relative magnitude observed in the stopping power curve. First, the narrow width of the O_2 $^2\Pi_g$ shape resonance reduces the vibrational excitation cross section, in spite of the long resonance lifetime (38). The large d-wave centrifugal barrier combined with the low energy of the shape resonance results in weak enhancement of stopping power relative to the N_2 and CO molecules. Therefore the stopping power of O_2 in the subexcitation range is actually comparable in magnitude to that of H_2 , where enhanced vibrational excitation is actually very weak. Second, the sharp peaks in the O_2 stopping power near 0.8 eV in Fig. 1 are strictly a consequence of the long shape resonance lifetime. Because the O_2^- ion is stable and forms well defined vibrational levels, the same peak positions (corresponding to the O_2^- vibrational levels) are observed in different vibrational decay channels of the neutral molecule (7, 38). The vibrational structure of the negative ion, therefore, is retained upon summing the alternative vibrational decay probabilities, weighted by their respective energy losses, according to Eq. (1). Thus in both the stopping power and the moderation rate (discussed below) the effective slowing down in this energy range is modulated according to this vibrational structure. Finally, note that beyond ~ 2 eV kinetic energy the stopping power of O_2 is completely dominated by the electronic contribution, corresponding to excitation of the $a^1\Delta_g$ and $b^1\Sigma_g^+$ electronic states. The excitation cross sections to these states are actually comparable to the vibrational cross sections on resonance ($\sim 1 \times 10^{-17}$ cm²); however, the energy losses are about an order of magnitude greater than vibrational losses (0.98 eV for the $a^1\Delta_g$ state, 1.65 eV for the $b^1\Sigma_g^+$ state (42)). This circumstance results in the large difference in $-dT/dx$ above and below the electronic threshold in O_2 .

Turning to the N_2 and CO curves in Fig. 1, the magnitude of $-dT/dx$ compared to H_2 and O_2 is much greater at the energy of the shape resonance. In N_2 and CO the shape resonance lifetime is comparable to the vibrational period of the molecule, and the resulting energy transfer to excitation of the nuclei is accordingly much greater than in H_2 and O_2 . The centrifugal barrier responsible for the $^2\Pi$ shape resonance in CO is weaker than N_2 , due to the lower symmetry and resultant admixture of p and d partial waves (7, 8). The vibrational excitation cross sections and stopping power for CO are therefore smaller than those for N_2 . In contrast to O_2 , the N_2 and CO stopping power curves *do not* reveal the underlying vibrational structure of the negative ion. Well defined vibrational states of the negative ion are not formed (so that peaks in the alternative decay channels of the neutral molecules do not coincide (7)), and the summing of vibrational decay probabilities according to Eq. (1) results in a relatively smooth stopping power curve.

A further significant aspect of the CO curve is its long tail as T approaches zero energy, lying above any of the other three curves in this range. Schulz (7) has dis-

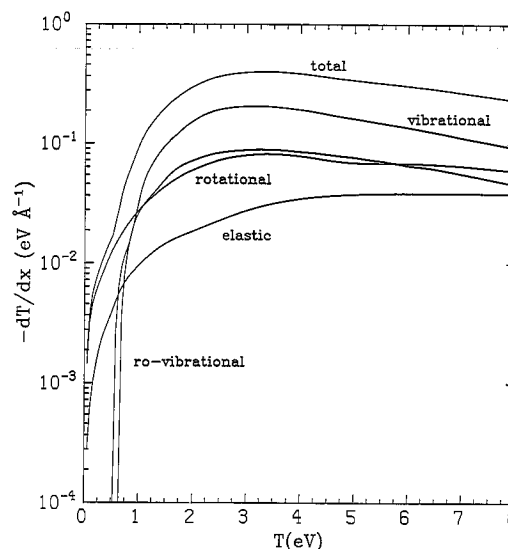


FIG. 2. Total electron stopping power and separate loss components for H_2 .

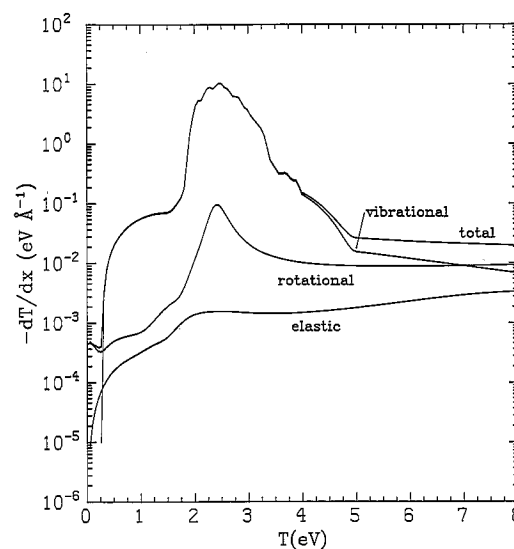
cussed this feature, specifically in the context of the $v = 1$ vibrational cross section, and so did Chandra (27) for the rotational cross sections. This long tail results from scattering by the weak permanent dipole and strong quadrupole fields present in CO and accordingly plays a special role in the calculated range and moderation time.

IV. SURVEY OF ENERGY LOSS MODES AND SLOWING-DOWN QUANTITIES

In this section we present and discuss graphs of the individual energy loss modes contributing to the total stopping power, and graphs of the slowing-down quantities defined in section II. Figures 2–9 display the main results of our calculations.

In Fig. 2 we display the separate vibrational, rotational, and elastic contributions to the stopping power for molecular hydrogen. The vibrational component dominates over most of the subexcitation range (as in the other three molecules), although for hydrogen the other loss modes constitute an appreciable fraction at any energy and dominate below ~ 0.5 eV kinetic energy. For hydrogen the contribution to slowing down from elastic collisions is actually comparable to the rotational and rovibrational components over the entire energy range. This is due to the small mass and large momentum-transfer (elastic) cross section for H_2 .

In Fig. 3 the separate contributions to the stopping power for molecular nitrogen are shown. The overwhelming influence of the $^2\Pi_g$ resonance in the vibrational contribution is apparent, although the detailed underlying vibrational structure has been smoothed by summing over alternative decay probabilities. In contrast to H_2 , the increased mass of N_2 causes the rotational and elastic components to differ substantially over large regions of the spectrum. Nonetheless, the breadth and intensity of the $^2\Pi_g$ resonance in the momentum-transfer cross section causes the rotational and elastic components to be comparable at 1–2 eV kinetic energy.


 FIG. 3. Total electron stopping power and separate loss components for N_2 .

Results for the separate components of the stopping power for carbon monoxide are shown in Fig. 4. Not surprisingly, they are very similar to the nitrogen curves (because of similarity of their electronic structure and shape resonances (7)), except for kinetic energies less than 1 eV. CO possesses a weak permanent dipole moment

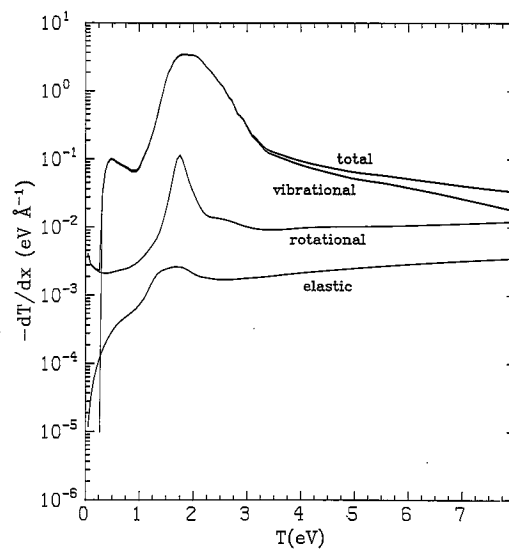


FIG. 4. Total electron stopping power and separate loss components for CO.

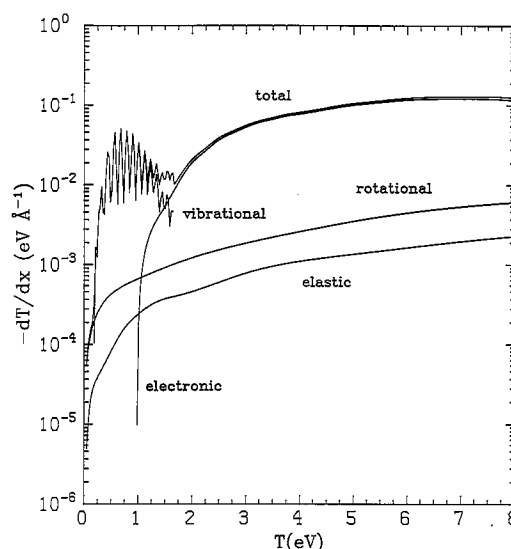


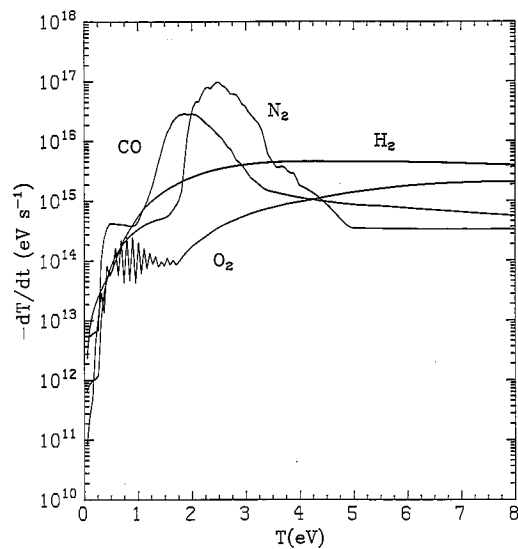
FIG. 5. Total electron stopping power and separate loss components for O_2 .

($0.044ea_0$) and a strong quadrupole moment ($-1.55ea_0^2$), and the long tails in the vibrational and rotational components result from strong scattering by these multipole moments.

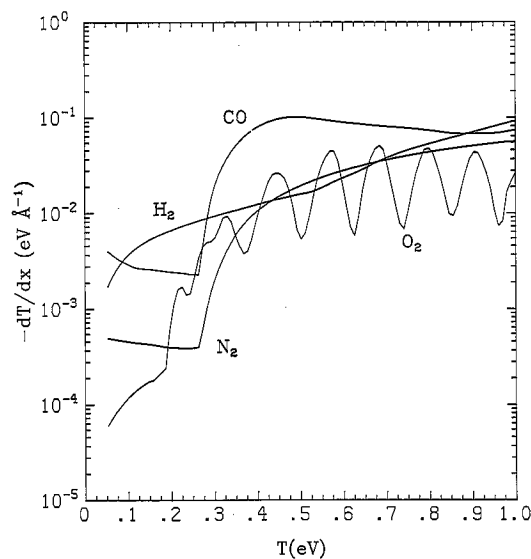
The separate contributions to the stopping power for molecular oxygen are shown in Fig. 5. As in the case of shape resonances in N_2 and CO , the vibrational contribution to $-dT/dx$ dominates over the other loss modes by two orders of magnitude in the region of the O_2 $^2\Pi_g$ shape resonance. Beyond the resonance the electronic component dominates all others by an even greater amount. We note that the cutoff of the vibrational component at ~ 1.6 eV is spurious, being due to lack of scattering data beyond this cutoff. Hake and Phelps (35) have reported values of the total vibrational excitation cross section up to 2.8 eV that are consistent in magnitude with the data employed in the present paper, but their data do not allow significant extension of the vibrational $-dT/dx$ curve. Since the stopping power is dominated by the electronic component in this region, we expect the total $-dT/dx$ curve as well as the other derived moderation quantities to be accurate within the CSDA.

Moderation Rate, Moderation Time, and Range

Shown in Fig. 6 is the moderation rate for each molecule, which is nearly identical to Fig. 1, except that the curves have been scaled by an increasing function $T^{1/2}$. In Fig. 7 we also show the stopping power on an expanded scale from 0–1 eV. These plots suggest that it is convenient to divide the subexcitation domain into three regions of classification: (a) the region below the first vibrational threshold, where rotational and elastic energy losses dominate; (b) the resonance region where molecular shape resonances greatly enhance the large losses to vibrational excitation, discussed


 FIG. 6. Electron moderation rate for H_2 , N_2 , CO , and O_2 .

previously; and (c) the postresonance region where direct vibrational energy transfers dominate. The behavior of slowing down parameters in regions (a) and (c) reflects mainly the long-range electron molecule interactions, discussed in more detail below. The cumulative integrals of the inverse stopping power and moderation rate in these

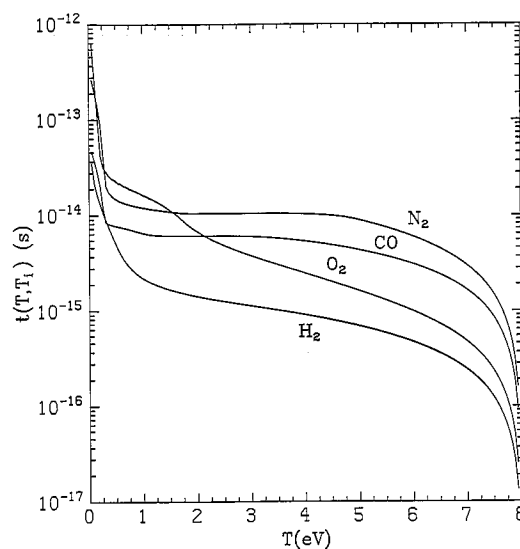

 FIG. 7. Total electron stopping power for H_2 , N_2 , CO , and O_2 in the range 0 to 1 eV.

three regions, respectively, determine the overall behavior of the range and moderation time of electrons. Mozumder and Magee (48) have stressed the importance of (a), the "subvibrational" range of subexcitation electrons with energies < 0.4 eV, in the context of solution phase radiation chemistry.

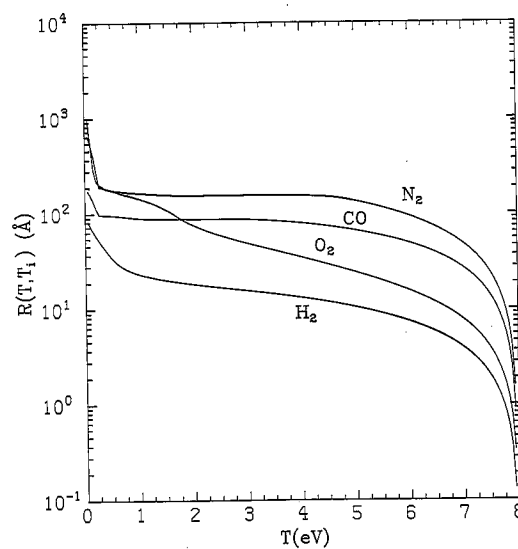
In the subvibrational region, the important parameters relevant to rotational cross sections (and stopping power) are the dipole and quadrupole moments and the non-spherical component α' of the dipole polarizability (49). In the pure Born-quadrupole approximation (50), the rotational excitation cross section is proportional to Q^2 . Near the minimum energy of $T = 0.054$ eV in the moderation rate, the ordering $\text{CO} > \text{N}_2 > \text{O}_2$ therefore reflects mainly a decreasing absolute value of quadrupole moments of the molecules. On the other hand, the stopping power of H_2 in this region is boosted relative to N_2 and O_2 because of the large rotational energy transfers which compete against the small excitation cross section ($\sim 10^{-2}$ Å), according to Eq. (1). Dalgarno and Moffet (26) also have derived a correction to the Born-quadrupole formula which accounts for polarization of the molecule by the electron and have shown that a cancellation occurs between these two contributions to the cross sections for molecules with negative quadrupole moment. This cancellation effect therefore implies an initially decreasing stopping power, which is apparent for N_2 and CO in Fig. 7. This decrease is visible in O_2 rotational cross sections only at a much lower kinetic energy (51).

In the postresonance region, the $\sigma_{0 \rightarrow 1}$ vibrational excitation cross section makes the dominant contribution to the electron stopping power. The important parameters which qualitatively govern the relative variation of the cross sections and stopping power are the internuclear distance dependence of the dipole ($D(R)$) and quadrupole ($Q(R)$) moments of the molecular field, and the polarizability $\alpha(R)$. Breig and Lin (49) have shown that, within the Born approximation, the $\sigma_{0 \rightarrow 1}$ vibrational cross section is proportional to the matrix elements $|(1|\alpha(R)|0)|^2$ and $|(1|Q(R)|0)|^2$. The matrix element of the polarizability (whose magnitude can be derived from Raman scattering intensities (52)) was shown to be the dominant contribution to direct vibrational excitation of H_2 , N_2 , and CO . Therefore, in the postresonance region of the stopping power or moderation rate, consideration of this factor alone can qualitatively account for the variation $\text{H}_2 > \text{CO} > \text{N}_2$. CO has an additional contribution from direct dipole excitation, which further enhances its moderation relative to N_2 . O_2 is again special because the electronic contribution to the moderation dominates over other components in the postresonance region, and comparing it with the other molecules on the basis of polarizability alone is not meaningful. It is interesting to note that, in the absence of shape resonance effects in N_2 and CO , the moderation rate of H_2 would significantly exceed the other molecules over nearly the entire subexcitation domain.

In Figs. 8 and 9 we compare our calculated moderation time and range for the four molecules. At the terminal energy $T = 0.054$ eV, the range and moderation time of O_2 exceed that of N_2 , CO , and H_2 . As the electron degrades into the subvibrational region, the rapid decrease of the stopping power and moderation rate obviously plays a decisive role in the ultimate slowing-down time and range of electrons in the gas. This observation is in agreement with the discussions of subexcitation electrons by Mozumder and Magee (48) and Christophorou *et al.* (53). In degrading through the resonance region, the shape resonances cause the cumulative integrals (3) and (4) to


 FIG. 8. Electron moderation time for H_2 , N_2 , CO , and O_2 .

increase only very slowly. That is, due to the shape resonances, the moderation time for a 6 eV subexcitation electron is nearly equivalent to that of a 1 eV electron in these molecules. Specifically the integrals of $(-dT/dx)^{-1}$ and $(-dT/dt)^{-1}$ in the vicinity of the N_2 and CO shape resonances are only 10–20% of their respective postresonance


 FIG. 9. Electron range for H_2 , N_2 , CO , and O_2 .

contributions. In contrast, the O_2 moderation time and range vary rapidly when the electron drops below the electronic threshold. The vibrational structure of the O_2 $^2\Pi_g$ shape resonance in the stopping power and moderation rate also enhances the integrated quantities below the electronic threshold.

V. SUMMARY AND CONCLUSION

We have compiled sets of cross sections for all energy loss processes in the subexcitation ranges of H_2 , N_2 , CO , and O_2 and have derived the stopping power and relevant moderation parameters for electron slowing down. A main purpose of this survey is to document *quantitatively* the effect that molecular shape resonances have on the degradation of electrons in the subexcitation region. The formation of a shape resonance and the resulting enhanced vibrational excitation is undoubtedly the principal loss mechanism for subexcitation electrons in the gas phase. Platzman (1) and his collaborators (4-6) have emphasized that the moderation rate $-dT/dt$ due to electronic excitation typically exceeds other loss modes by two or three orders of magnitude; we note here that molecular shape resonances enhance the stopping power over the nonresonant background by a similar amount. In addition, the enhanced loss due to the shape resonances may actually be *comparable* to the electronic loss. The resonances accordingly cause a substantial reduction in the average moderation time and range of slow electrons, prior to their degradation into the subvibrational region. The rapid decrease of stopping power below vibrational thresholds is seen to greatly enhance the moderation time and range of the molecules; this important aspect of subexcitation electrons was indicated long ago (48, 53).

Similar studies should extend calculations of the stopping power to other molecules and higher kinetic energies, as more collision data become available. In particular they should assess the importance of additional resonantly enhanced vibrational excitation (54), which occurs at ~ 15 -25 eV kinetic energy in many molecules, and resonant and nonresonant contributions from electronic excitations.

ACKNOWLEDGMENTS

We are indebted to Professor U. Fano and Dr. Mitio Inokuti for discussions leading to the development of this paper and for their critical readings of the manuscript. This work was supported by the Office of Health and Environmental Research, U.S. Department of Energy, under contract DE-AC02-84ER60194.

RECEIVED: May 20, 1986; REVISED: October 23, 1986

REFERENCES

1. R. L. PLATZMAN, Subexcitation electrons. *Radiat. Res.* **2**, 1-7 (1955).
2. M. INOKUTI, Inelastic collisions of fast charged particles with atoms and molecules—The Bethe theory revisited. *Rev. Mod. Phys.* **43**, 297-347 (1971).
3. U. FANO, Penetration of protons, alpha particles, and mesons. *Annu. Rev. Nucl. Sci.* **13**, 1-66 (1963).
4. M. INOKUTI, R. L. PLATZMAN, and K. TAKAYANAGI, Role of dissociative electron attachment in radiation chemistry. In *Radiological Physics Division Annual Report No. ANL-7220*, pp. 11-12. Argonne National Laboratory, Argonne, IL, 1966.
5. M. INOKUTI, Radiation physics as a basis of radiation chemistry and biology. In *Applied Atomic Collision Physics, Vol. 4, Condensed Matter* (S. Datz, Ed.), pp. 179-236. Academic Press, New York, 1983.

6. K. TAKAYANAGI, Introduction to electron-molecule collisions. In *Electron-Molecule Collisions* (I. Shimamura and K. Takayanagi, Eds.), pp. 1-87. Plenum, New York, 1984.
7. G. J. SCHULZ, Resonances in electron impact on diatomic molecules. *Rev. Mod. Phys.* **45**, 423-486 (1973).
8. N. F. LANE, The theory of electron-molecule collisions. *Rev. Mod. Phys.* **52**, 29-119 (1980).
9. G. CSANAK, D. C. CARTWRIGHT, S. K. SRIVASTAVA, and S. TRAJMAR, Elastic scattering of electrons by molecules. In *Electron-Molecule Interactions and Their Applications* (L. G. Christophorou, Ed.), Vol. I, pp. 1-153. Academic Press, New York, 1984.
10. S. TRAJMAR and D. C. CARTWRIGHT, Excitation of molecules by electron impact. In *Electron-Molecule Interactions and Their Applications* (L. G. Christophorou, Ed.), Vol. I, pp. 155-249. Academic Press, New York, 1984.
11. J. B. HASTED and D. MATHUR, Electron-molecule resonances. In *Electron-Molecule Interactions and Their Applications* (L. G. Christophorou, Ed.), Vol. I, pp. 403-475. Academic Press, New York, 1984.
12. J. L. DEHMER, Shape-resonances in molecular fields. In *Resonances in Electron-Molecule Scattering, Van der Waals Complexes, and Reactive Chemical Dynamics* (D. G. Truhlar, Ed.), pp. 139-163. American Chemical Society, Washington, DC, 1984.
13. L. SANCHE and M. MICHAUD, Vibrational-librational excitation and shape resonances in electron scattering from condensed N_2 , CO, O_2 , and NO. In *Resonances in Electron-Molecule Scattering, Van der Waals Complexes, and Reactive Chemical Dynamics* (D. G. Truhlar, Ed.), pp. 211-228, and references quoted therein. American Chemical Society, Washington, DC, 1984.
14. U. FANO, Degradation and range straggling of high-energy radiations. *Phys. Rev.* **92**, 328-349 (1953).
15. L. V. SPENCER and U. FANO, Energy spectrum resulting from electron slowing down. *Phys. Rev.* **93**, 1172-1181 (1954).
16. U. FANO and J. A. STEPHENS, Slow electrons in condensed matter. *Phys. Rev. B* **34**, 438-441 (1986).
17. D. A. DOUTHAT, Energy deposition and electron energy degradation in molecular hydrogen. *J. Phys. B* **12**, 663-678 (1979).
18. D. A. DOUTHAT, Electron terminal times in irradiated helium and hydrogen. *J. Chem. Phys.* **79**, 4599-4601 (1983).
19. A. GILARDINI, *Low Energy Electron Collisions in Gases*, pp. 18-25. Wiley, New York, 1972.
20. D. K. GIBSON, Rotational cross sections for H_2 and D_2 . *Aust. J. Phys.* **23**, 683-696 (1970).
21. T. W. SHYN and W. E. SHARP, Angular distributions of electrons elastically scattered from H_2 . *Phys. Rev. A* **24**, 1734-1740 (1981).
22. F. LINDER and H. SCHMIDT, Rotational and vibrational excitation of H_2 by slow electron impact. *Z. Naturforsch.* **26**, 1603-1617 (1971).
23. H. EHRHARDT, L. LANGHANS, F. LINDER, and H. S. TAYLOR, Resonance scattering of slow electrons from H_2 and CO angular distributions. *Phys. Rev.* **173**, 222-230 (1968).
24. T. W. SHYN and G. R. CARIGNAN, Angular distribution of electrons elastically scattered from gases: 1.5-400 eV on N_2 . II. *Phys. Rev. A* **22**, 923-929 (1980).
25. A. G. ENGELHARDT, A. V. PHELPS, and C. G. RISK, Determination of momentum transfer and inelastic collision cross sections for electrons in nitrogen using transport coefficients. *Phys. Rev.* **135**, A1566-A1574 (1964).
26. A. DALGARNO and R. J. MOFFET, The rotational excitation of molecular nitrogen by slow electrons. *Proc. Natl. Acad. Sci. India* **33**, 511-521 (1963).
27. N. CHANDRA and P. G. BURKE, Rotational excitation cross sections for e^- - N_2 scattering. *J. Phys. B* **6**, 2355-2357 (1973).
28. G. J. SCHULZ, Vibrational excitation of N_2 , CO, and H_2 by electron impact. *Phys. Rev. A* **135**, 988-994 (1964).
29. K. JUNG, TH. ANTONI, R. MULLER, K-H KOCHER, and H. EHRHARDT, Rotational excitation of N_2 , CO and H_2O by low-energy electron collisions. *J. Phys. B* **15**, 3532-3555 (1982).
30. H. TANAKA, Y. YAMAMOTO, and T. OKADA, Electron impact cross sections for $v = 0 \rightarrow 1$. Vibrational excitation of N_2 at electron energies from 3 to 30 eV. *J. Phys. B* **14**, 2081-2088 (1981).
31. H. EHRHARDT and K. WILLMAN, The angular dependence of resonance scattering of slow electrons in N_2 . *Z. Phys.* **204**, 462-473 (1967).

32. J. E. LAND, Electron scattering cross sections for momentum transfer and inelastic excitation in carbon monoxide. *J. Appl. Phys.* **49**, 5716-5721 (1978).
33. N. CHANDRA, Low energy electron scattering from CO. II. Ab initio study using the frame transformation theory. *Phys. Rev. A* **16**, 80-108 (1977).
34. A. CHUTJIAN and H. TANAKA, Electron impact cross sections for $v = 0 \rightarrow 1$ vibrational excitation in CO at electron energies of 3 to 100 eV. *J. Phys. B* **13**, 1901-1908 (1980).
35. R. D. HAKE, JR., and A. V. PHELPS, Momentum transfer and inelastic collision cross sections for electrons in O₂, CO, and CO₂. *Phys. Rev.* **158**, 70-84 (1967).
36. T. W. SHYN and W. E. SHARP, Angular distributions of electrons elastically scattered from O₂: 2.0-200 eV. *Phys. Rev. A* **26**, 1369-1372 (1982).
37. YU. D. OKSYUK, Excitation of the rotational levels of diatomic molecules by electron impact in the adiabatic approximation. *Sov. Phys. JETP* **22**, 873-881 (1966).
38. F. LINDER and H. SCHMIDT, Experimental study of low energy e-O₂ collision processes. *Z. Naturforsch* **26**, 1617-1625 (1971).
39. S. TRAJMAR, D. C. CARTWRIGHT, and W. WILLIAMS, Differential and integral cross sections for the electron-impact excitation of the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states of O₂. *Phys. Rev. A* **4**, 1482-1492 (1971).
40. S. TRAJMAR, D. F. REGISTER, and A. CHUTJIAN, Electron scattering by molecules. II. Experimental methods and data. *Phys. Rep.* **87**, 219-356 (1983).
41. E. CHANG and U. FANO, Theory of electron-molecule collisions by frame transformations. *Phys. Rev. A* **6**, 173-185 (1972).
42. K. P. HUBER and G. HERZBERG, *Constants of Diatomic Molecules*. Van Nostrand-Reinhold, New York, 1979.
43. M. ALLEN, Experimental observation of structures in the energy dependence of vibrational excitation in H₂ by electron impact in the $2\Sigma_u^+$ resonance region. *J. Phys. B* **18**, L451-L455 (1985).
44. H. NISHIMURA, A. DANJO, and H. SUGAHARA, Differential cross sections of electron scattering from molecular hydrogen. I. Elastic scattering and vibrational excitation ($X^1\Sigma_g^+$, $v = 0 \rightarrow 1$). *J. Phys. Soc. Jpn.* **54**, 1757-1768 (1985).
45. B. I. SCHNEIDER, M. LE DOURNEUF, and V. K. LAN, Resonant vibrational excitation of N₂ by low-energy electrons: An *ab initio* R-matrix calculation. *Phys. Rev. Lett.* **43**, 1926-1929 (1979).
46. C. SZMYTKOWSKI and M. ZUBEK, Absolute total electron scattering cross sections of CO, CO₂, and OCS in the low energy region. *Chem. Phys. Lett.* **57**, 105-108 (1978).
47. L. G. CHRISTOPHOROU, The lifetimes of metastable negative ions. *Adv. Electron. Electron Phys.* **46**, 55-129 (1978).
48. A. MOZUMDER and J. L. MAGEE, Theory of radiation chemistry. VIII. Ionization of nonpolar liquids by radiation in the absence of external electric field. *J. Chem. Phys.* **47**, 939-945 (1967).
49. E. L. BREIG and C. C. LIN, Vibrational excitation of diatomic molecules by electron impact. *J. Chem. Phys.* **43**, 3839-3845 (1965).
50. E. GERJUOY and S. STEIN, Rotational excitation by slow electrons. *Phys. Rev.* **97**, 1671-1679 (1955).
51. S. GELTMAN and K. TAKAYANAGI, Excitation of molecular rotation by slow electrons. II. *Phys. Rev.* **143**, 25-30 (1966).
52. E. J. STANSBURY, M. F. CRAWFORD, and H. L. WELSH, Determination of rates of change of polarizability from Raman and Rayleigh intensities. *Can. J. Phys.* **31**, 954-961 (1953).
53. L. G. CHRISTOPHOROU, K. S. GANT, and J. K. BAIRD, Slowing down of subexcitation electrons in polyatomic gases. *Chem. Phys. Lett.* **30**, 104-108 (1975).
54. D. DILL and J. L. DEHMER, Total elastic electron scattering cross section for N₂ between 0 and 1000 eV. *Phys. Rev. A* **16**, 1423-1431 (1977).