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Coherent resonance and dipole scattering in rotational excitation of molecules by slow electrons

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We present a new approach to rotational-vibrational excitation of molecules by slow electrons, incorporating the shape resonance, the dipole interaction, and the interference between their amplitudes. Excellent agreement is found with the high-resolution differential-cross-section data in CO for vibrational excitation and the simultaneous excitation of individual rotational branches. Accurate state-to-state integral cross sections are given for CO at the resonance energy of 1.8 eV.

Rotational and vibrational excitation of molecules by electrons in the eV and sub-eV range is one of the dominant energy-transfer processes in situations where the energy distributions of the electrons thermalize rather rapidly. Examples are penetration of fast charged particles through dense gases, molecular lasers, planetary ionospheres, and explosions, etc. In favorable cases, electron-swarm experiments[1] can yield accurate rotational as well as diffusion cross sections.[2] With high-resolution electron spectrometers, crossed-beam experiments can now reach down to incident energies of 50 meV, with resolution of state-to-state rotational cross sections[3] in H_2. In other molecules, line-shape analysis leads to reliable cross sections for different ΔJ transitions.[4] Since beam experiments measure the energy and the scattering angle dependencies, the results exhibit detailed information on the reaction mechanisms.

Recent reviews of the theory of electron-molecule collisions[5-7] disclose a dearth of *ab initio* calculations of simultaneous rotational and vibrational cross sections. Thus, it is desirable to focus on excitation mechanisms in a semiempirical theoretical approach. Basically, excitation cross sections become large when the colliding electron is trapped in a short lived negative ion state of the molecule (resonance) or when a nonresonant but long-range interaction between the electron and molecule is present.[4-8] However, when both reaction mechanisms are present, they can interfere. This feature has been found to be important in other theories such as the two-potential theory[9] for the intermediate energy range. For the low-energy regime, the present work shows how the interference as well as the two mechanisms themselves can be treated in a general situation. For an infrared-active vibrational mode, the long-range interaction is dominated by the dipole potential. We will show how spectroscopic information such as the dipole transition moment enters into electron scattering. In the frame transformation theory,[10] the short-range resonance mechanism is more conveniently described in the molecular frame while the long-range dipole potential is more suitably depicted in the laboratory frame.[6] These concepts have now been combined into a new theory. Details and applications to polyatomic molecules are given elsewhere.[11] Here, we will illustrate its application to rovibrational excitation of CO at the resonance energy of 1.8 eV, where detailed rotational branch differential cross sections are available.[4]

In the previous work,[10] it has been shown that the rovibrational differential cross section (DCS) can be expressed as a single sum over the angular momentum transfer j. In infrared-active vibrational modes, the dominant long-range dipole potential carries one unit of angular momentum, i.e., $j=1$ (just like the photon). Therefore, only in the $j=1$ term does the dipole amplitude $f_D(j)$ interfere with the resonant amplitude $f_R(j)$. Thus the state-to-state $J \rightarrow J'$ DCS for a dipole rotational transition is given by

$$\frac{d\sigma_{JJ'}}{d\Omega} = A_J^1 |f_R(1) + e^{i\chi} f_D(1)|^2 + \sum_{j\neq 1} A_J^j |f_R(j)|^2 \ , \quad (1)$$

where $A_J^j = (J,\Lambda;j,\Lambda'-\Lambda|J',\Lambda')^2$, and in particular A_J^j is essentially the Hönl-London factor for line intensity from spectroscopy,[12] and χ is the relative phase. Usually the rotational states are not fully resolved in experiments, so the vibrational DSC (summed over final and averaged over initial rotational states) is given by

$$\frac{d\sigma_v}{d\Omega} = \frac{d\sigma_R}{d\Omega} + |f_D(1)|^2 + 2\cos\chi\, f_R(1) f_D(1) \ . \quad (2)$$

At lower energies, it has been shown that the measured vibrational DCS is well described by the dipole interaction in the Born approximation.[13] Then the scattering amplitude is found to be

$$f_D(1) = (2D/k)(\tilde{k}/3)^{1/2}(1+\tilde{k}^2 - 2\tilde{k}\cos\theta)^{-1/2} \ , \quad (3)$$

where D is the vibrational transition moment to a particular vibrational mode. Using atomic units throughout, k is the momentum of the incident electron, and $\tilde{k}$ the ratio of the final to the initial momenta.

In CO, the vibrational transition is of the type $\Sigma^+ \rightarrow \Sigma^+$; therefore, A_J is simply $J/(2J+1)$ for the P branch ($\Delta J = -1$), or $(J+1)/(2J+1)$ for the R branch ($\Delta J = +1$). For the $v=0 \rightarrow 1$ vibrational excitation under consideration, D is found from infrared intensity measurements[14] to be 0.0421 ea_0. The $^2\Pi$ resonance in CO has been found to peak at 1.8 eV, where $k=0.364$ and $\tilde{k}=0.923$. For rotational transitions $\Delta J = \pm 1$, the resonant cross section has been shown[15] to contain only two terms corresponding to $j=1$ and 3,

$$f_R(1) = (R\sin 2\beta/k)\,[3\tilde{k}(1+5\cos\theta+3\cos^2\theta-9\cos^3\theta)/10]^{1/2} \ , \quad (4)$$

and

$$f_R(3) = (R\sin 2\beta/k)\,[\tilde{k}(4-5\cos\theta+2\cos^2\theta-\cos^3\theta)/28]^{1/2} \ , \quad (5)$$

using the high-J approximation.[16] In Eqs. (4) and (5), R is the square root of the resonant vibrational cross section,

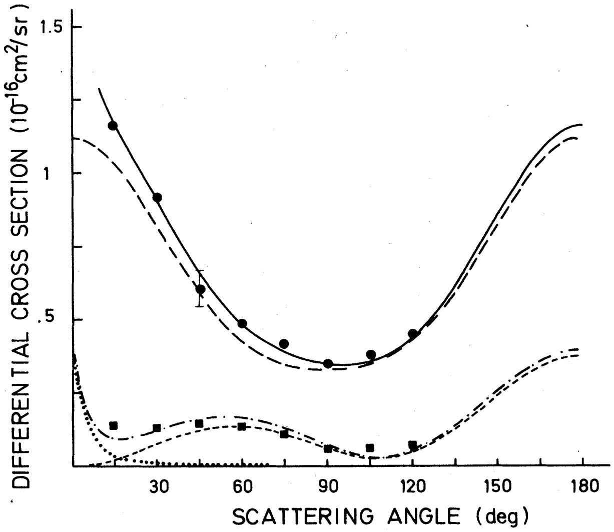

FIG. 1. Differential cross sections of e-CO ($v=0\rightarrow 1$) at 1.8 eV. Top curves are summed over rotations: ●●●, experiment; ——, full theory; – – –, resonance only. Bottom curves are for the $\Delta J=1$ branch: ■ ■ ■, experiment; – · – ·, full theory; – – –, resonance only; and · · · ·, dipole only.

and $\tan\beta$ is the mixing parameter between the $p\pi$ and the $d\pi$ partial waves. Together with χ, R and β will be regarded as fitting parameters in this work. Substituting these and Eq. (3) into Eq. (1), we obtain the DCS for the $\Delta J=\pm 1$ rotational branches in our new theory. Similarly Eq. (2) becomes the new expression for the vibrational DCS, while the old one based on the resonance alone[15] is given below.

$$\frac{d\sigma_R}{d\Omega}=(\tilde{k}R^2/4k^2)\left[\tfrac{3}{20}(1+7\cos^2\theta)(1+\cos2\beta)^2+\tfrac{5}{28}(3-9\cos^2\theta+14\cos^4\theta)(1-\cos2\beta)^2+\tfrac{3}{14}(3+5\cos^2\theta)\sin^2 2\beta\right] . \tag{6}$$

As a matter of fact Eq. (6) with $R=0.76$ and $\cos2\beta=0.15$ was found to fit[16] the measured vibrational DCS given by circles in Fig. 1. However, the pure resonance expression for the $\Delta J=+1$ DCS fell far short of the corresponding data (squares).

In the complete expression for the vibrational DCS, Eq. (2), the value of the additional parameter χ can be determined to be 42° by fitting the R-branch DCS data with the old values of R and $\cos2\beta$. After minor adjustments, a better fit with the vibrational DCS data is obtained (solid curve in Fig. 1). As expected, R and $\cos2\beta$ only change minutely to 0.73 and 0.1, respectively. For comparison, Eq. (6) with the same values for R and $\cos2\beta$ is shown as the dashed curve. We see that the present theory improves slightly the agreement with experiment by raising the forward angle DCS by about 10%.

For the DCS of the R branch, the new result given by Eq. (1) shown by the dash-dot curve is now in accordance with experiment. The improvement over the old theory is not sensitive to the value of χ and is the most dramatic in the small angles, where they differ by more than a factor of 2. Not shown in Fig. 1 are the other rotational branch DCS's, $\Delta J=0$, ± 2, ± 3, and ± 4. Since they are essentially unaffected by the dipole potential, their agreement with experiment is just as good as in our previous work.[16]

TABLE I. State-to-state integral rotational cross sections in 10^{-16} cm^2. Results are displayed for the electron energy of 1.8 eV and for the $v=0\rightarrow 1$ transition in CO. J is the initial and ΔJ the change in the rotational quantum number. The high J approximation is used for $J=10$ and ∞.

J \ ΔJ	0	1	2	3	4
0	1.84	2.47	0.85	1.29	0.60
1	2.18	2.20	0.78	0.74	0.34
2	2.26	1.82	0.59	0.62	0.27
10	2.14	1.55	0.45	0.47	0.20
∞	2.14	1.48	0.41	0.40	0.17

With the excellent fit, we can now determine accurate state-to-state cross sections from the new theory. For convenience in applications, we discuss next integral cross sections. Fortunately, the general expressions for resonant scattering have already been presented.[16] So we only need to give the additional nonresonant contributions to $\sigma(\Delta J=\pm 1)$,

$$\sigma(\Delta J=\pm 1)=\sigma_R(\Delta J=\pm 1)+A_J(\sigma_B+\sigma_I) . \tag{7}$$

The Born term has been found[17] to be

$$\sigma_B=(8\pi D^2/3k^2)\ln[(1+\tilde{k})/(1-\tilde{k})] , \tag{8}$$

and the interference term is

$$\sigma_I=2\cos\chi\int f_R(1)f_B(1)d\Omega . \tag{9}$$

For the situation at hand, σ_B and σ_I are evaluated to be 0.101 and 0.427 in units of 10^{-16} cm^2, respectively.

Finally, we give the formulas for calculating the state-to-state $v=0\rightarrow 1$ cross sections at 1.8 eV, in 10^{-16} cm^2,

$$\sigma(\Delta J=\text{even})=1.845\delta_{J,J'}+0.849(J,0;\,2,0|J',0)^2+0.604(J,0;\,4,0|J',0)^2 , \tag{10}$$

$$\sigma(\Delta J=\text{odd})=2.568(J,0;\,1,0|J',0)^2+1.293(J,0;\,3,0|J',0)^2 . \tag{11}$$

$(j_1,m_1;\,j_2,m_2|j_3,m_3)$ is the Clebsch-Gordan coefficient. In Table I, we show some specific state-to-state cross sections. Note that the values for $\Delta J=0$ and $+1$ are substantially larger than the others. The former is expected because the process is "elastic," and the latter is enhanced particularly by the interference term. The cross section summed over all final rotational states has a value of 7.05×10^{-16} cm^2 and is independent of the initial rotational state.

The procedure we have applied to CO is quite general, and is particularly important in the infrared-active modes of polyatomic molecules.[11] Details on CO_2 and C_2H_2 will be reported later.

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