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Theory of angular distributions of electrons resonantly scattered by molecules. II. Vibrational and rotational excitation of CO

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The experimental data for vibrational excitation of CO by electrons with incident energy of 1.8 eV are analyzed using a recent theory. Though the theoretical expression for resonant angular distributions contains only one parameter, it fits the data very well allowing accurate determination of the parameter's value. Using this value, all rotational cross sections within the vibrational band are calculated.

A new theory for angular distributions of low-energy electrons resonantly scattered by diatomic molecules has recently been developed[1] (referred to here as I). In application to homonuclear molecules, the expressions are equivalent to those of O'Malley and Taylor (OT)[2] and those of Read.[3] However, its application to heteronuclear molecules produces expressions different from the others. In particular our expressions contain only the mixing parameter, while those of Read contain two parameters, and apparently so do those of OT in the same approximation. In this work, we apply this theory to CO where good data are available from the work of Ehrhardt, Langhans, Linder, and Taylor[4] (ELLT).

These data show that for vibrationally elastic scattering, the angular distributions vary greatly depending on the incident energy in the range 1.0–3.5 eV. On the other hand, for vibrational excitation to the final state $v=1$ up to $v=6$, the angular distributions are remarkably constant for 1.5–3.0 eV. These observations strongly indicate that vibrational excitation in CO is dominated by a resonance with negligible potential or background scattering. Previous analyses[2,3] show that the resonance is of $^2\Pi$ symmetry. Hence we have $\Lambda=1$, and the lowest two partial waves are $l_0=1$ and $l=2$. Substituting these values into the previously obtained expression for the angular distributions, I(23), we obtain

$$\frac{d\sigma}{d\Omega}(v \leftarrow v_0)=4\pi\sigma_{vv_0}(1)\left(\sum_{j_t=\text{even}}\left[(1+\cos 2\beta)^2(11,j_t0|11)^2\Theta(j_t;1111\theta)+(1-\cos 2\beta)^2(21,j_t0|21)^2\Theta(j_t;2222\theta)\right]\right.$$
$$\left.+\sum_{j_t=\text{odd}}2\sin^2 2\beta(21,j_t0|11)^2\Theta(j_t;1122\theta)\right). \tag{1}$$

In Eq. (1), $\sigma_{vv_0}(1)$ may be regarded as a normalization constant, and $\tan\beta$ is the mixing parameter whose value may be determined from an *a priori* calculation or from fitting to the experimental data. The quantities $(\ldots,\ldots|\ldots)$ are Clebsch-Gordan coefficients and $\Theta(j_t;l_0l_0'll'\theta)$ are standard angular functions. Utilizing the Tables in I, we find[5]

$$\frac{d\sigma}{d\Omega}(v \leftarrow v_0)=4\pi\sigma_{vv_0}(1)\left[\tfrac{3}{20}(1+7\cos^2\theta)(1+\cos 2\beta)^2+\tfrac{5}{28}(3-9\cos^2\theta+14\cos^4\theta)(1-\cos 2\beta)^2+\tfrac{3}{14}(3+5\cos^2\theta)\sin^2 2\beta\right]. \tag{2}$$

The first term gives the pure $p\pi$ contribution, and is identical to the theoretical curve in ELLT where only this lowest partial wave is considered. The second term gives the pure $d\pi$ contribution, and is identical to the ELLT theoretical curve for the $^2\Pi_g$ resonance in N_2. The last term has both $p\pi$ and $d\pi$ waves, i.e., p in, d out amplitude squared and vice versa, but is not an interference term, as is evident from the fact that it contains only even powers of $\cos\theta$. The results of this work differ from those of Read in the absence of a second parameter which determines the asymmetry about 90°. For comparison, Read's expression for a π resonance is

$$\begin{aligned}\frac{d\sigma}{d\Omega} \propto\ & (0.033\,33+0.085\,71\rho+0.200\,00\rho^2)\\ & +(0.233\,33+0.142\,86\rho-0.128\,57\rho^2)\cos^2\theta\\ & +0.200\,00\rho^2\cos^4\theta-0.285\,71\rho\cos^2\gamma\cos\theta\\ & +0.742\,86\rho\cos^2\gamma\cos^3\theta\ . \end{aligned} \tag{3}$$

He obtained best fit with experiment with $\rho=1.0$ and $\cos^2\gamma=0$ (and with $\rho=1.0$ and $\cos^2\gamma=0.25$ a close second-best fit).

In Fig. 1, we show the experimental data of ELLT for CO $v=0\rightarrow1$ vibrational excitation at an incident energy of 1.8 eV. With all theoretical curves normalized to the experiment at 90°, the parameter-free expression of OT (dashed line) clearly does not fit well.[2] The best fit of Read, Eq. (3) with $\rho=1.0$ and $\cos^2\gamma=0$ is shown as the dash-dot line. It can also be obtained from Eq. (2) with $\cos2\beta=0.25$. The solid line shows the result for Eq. (2) with $\cos2\beta=0.31$, and clearly both curves fit the experimental data very well. Since the small-angle data are less accurate and more prone to contain nonresonant contributions, we consider the curve with $\cos2\beta=0.25$ a better fit.

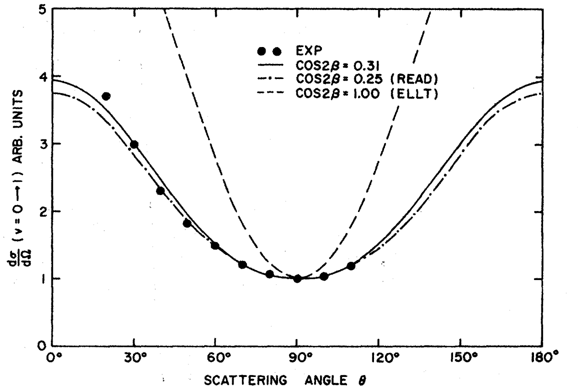

FIG. 1. Angular distributions for vibrational excitation of CO by electrons at 1.8 eV. All curves are normalized to 1 at 90°.

As discussed in I, we may now proceed to evaluate the individual rotational-vibrational cross sections from I(21). We find

$$\begin{aligned}\frac{d\sigma}{d\Omega}(jv\leftarrow j_0v_0)=4\pi\sigma_{vv_0}(1)\Bigg(\sum_{j_t=\text{even}} & (j_00,j_t0\,|\,j0)^2\big[(1+\cos2\beta)^2(11,j_t0\,|\,11)^2\Theta(j_t;1111\theta)\\ & +(1-\cos2\beta)^2(21,j_t0\,|\,21)^2\Theta(j_t;2222\theta)\\ & +2(1+\cos2\beta)(1-\cos2\beta)(11,j_t0\,|\,11)(21,j_t0\,|\,21)\Theta(j_t;1212\theta)\big]\\ & +\sum_{j_t=\text{odd}}(j_00,j_t0\,|\,j0)^2\big[2\sin^22\beta(21,j_t0\,|\,11)\Theta(j_t;1122\theta)\\ & -2\sin^22\beta(11,j_t0\,|\,21)(21,j_t0\,|\,11)\Theta(j_t;1221\theta)\big]\Bigg)\,. \end{aligned} \tag{4}$$

Similar to Eq. (2), the first term comes from p wave, the second d wave and the fourth the same mixture (not interference) of p and d waves. The third and fifth terms are new and represent true interference effects, with the third showing pure p interfering with pure d amplitudes while the fifth showing p in, d out interfering with d in, p out amplitudes (and vice versa). As shown in I, these two terms will cancel out only when one sums over rotational states. Utilizing the tables in I, we have the following: For $\Delta j=0$,

$$\begin{aligned}\frac{d\sigma}{d\Omega}(jv\leftarrow jv_0)=4\pi\sigma_{vv_0}(1)\big\{ & (j0,00\,|\,j0)^2\big[(1+\cos2\beta)^2\cos^2\theta+(1-\cos2\beta)^2(0.25-1.5\cos^2\theta+2.25\cos^4\theta)\\ & +2(1+\cos2\beta)(1-\cos2\beta)(-0.5\cos\theta+1.5\cos^3\theta)\big]\\ & +(j0,20\,|\,j0)^2\big[(1+\cos2\beta)^2(0.15+0.05\cos^2\theta)\\ & +(1-\cos2\beta)^2\,0.071(1.429-3.214\cos^2\theta+3.214\cos^4\theta)\\ & +2(1+\cos2\beta)(1-\cos2\beta)(-0.085)(0.423\cos\theta+1.268\cos^3\theta)\big]\\ & +(j0,40\,|\,j0)^2(1-\cos2\beta)^2\times0.127(1.446+0.965\cos^2\theta+0.161\cos^4\theta)\big\}\ . \end{aligned} \tag{5}$$

For $\Delta j = 1$,

$$\frac{d\sigma}{d\Omega}\,(j\pm 1v \leftarrow jv_0) = 4\pi\sigma_{vv_0}(1)\{(j\,0,\,10\,|\,j\pm 10)^2\,2\sin^2 2\beta[0.3(0.5+1.5\cos^2\theta)+0.387(1.936\cos\theta-3.486\cos^3\theta)]$$
$$+(j\,0,\,30\,|\,j\pm 10)^2\,2\sin^2 2\beta[0.086(2+\cos^2\theta)+0.111(-1.936\cos\theta-0.387\cos^3\theta)]\}\,. \quad (6)$$

For $\Delta j = 2$ and 4, we use Eq. (5) replacing the Clebsch-Gordan coefficient in each term by the appropriate one, and similarly for $\Delta j = 3$, we use Eq. (6) with the same replacement. Cross sections with $\Delta j > 4$ are zero in our model, and expected to be negligibly small in practice.

Specifically we consider the case $j = 0$, and taking $\cos 2\beta = 0.25$, we find

$$\frac{d\sigma}{d\Omega}\,(0\leftarrow 0) = 4\pi\sigma_{vv_0}(1)[0.14-0.94\cos\theta +0.72\cos^2\theta+2.81\cos^3\theta +1.27\cos^4\theta], \quad (7)$$

$$\frac{d\sigma}{d\Omega}\,(1\leftarrow 0) = 4\pi\sigma_{vv_0}(1)1.76[0.15+0.75\cos\theta +0.45\cos^2\theta-1.35\cos^3\theta], \quad (8)$$

$$\frac{d\sigma}{d\Omega}\,(2\leftarrow 0) = 4\pi\sigma_{vv_0}(1)[0.29-0.07\cos\theta-0.05\cos^2\theta -0.20\cos^3\theta+0.18\cos^4\theta], \quad (9)$$

$$\frac{d\sigma}{d\Omega}\,(3\leftarrow 0) = 4\pi\sigma_{vv_0}(1)\,1.76[0.17-0.22\cos\theta +0.09\cos^2\theta-0.04\cos^3\theta], \quad (10)$$

and

$$\frac{d\sigma}{d\Omega}\,(4\leftarrow 0) = 4\pi\sigma_{vv_0}(1)[0.10+0.07\cos^2\theta +0.01\cos^4\theta]. \quad (11)$$

Equations (7)–(11) are shown in Fig. 2, together with their sum which is also given by Eq. (2). As noted in I, the elastic cross section given by Eq. (7) shows a large forward peak while the inelastic one given by Eq. (8) shows a backward peak. The sum is symmetric about 90°. Results for other values of j are similar, with the elastic cross sections a little larger, and the inelastic ones smaller.

To illustrate the dependence on rotational quantum numbers, we show the integrated cross sections in Table I. These cross sections may be normalized to the experimental data of ELLT for $v = 0 \to 1$ at 1.8 eV by multiplying by 0.9×10^{-16} cm^2. We see that the rotationally elastic cross sections (given by the diagonal) are indeed larger than the one for $j_0 = 0$. Similarly the inelastic ones are smaller (though the superelastic ones are larger) than for the case $j_0 = 0$. The last column provides the classical limit cross sections for large values of j. Note that the first row provides a numerical check of I(28) or alternatively I(29).

$$\text{Ratio}\,\frac{(\Delta j\ \text{even})}{(\Delta j\ \text{odd})} = 1+2\,\text{ctn}^2 2\beta = 1.13. \quad (12)$$

Other rows may be used for the same purpose with trivial extension of the table.

Returning to Eq. (2), we now see that for homonuclear diatomic molecules, $|\cos 2\beta| = 1$, hence $\sin 2\beta = 0$. Consequently $\Delta j =$ odd transitions represented by the last term must vanish. In particular, for a Πg resonance as in N_2, $\cos 2\beta = -1$, while for a Πu resonance $\cos 2\beta = +1$. However, for a hetero-

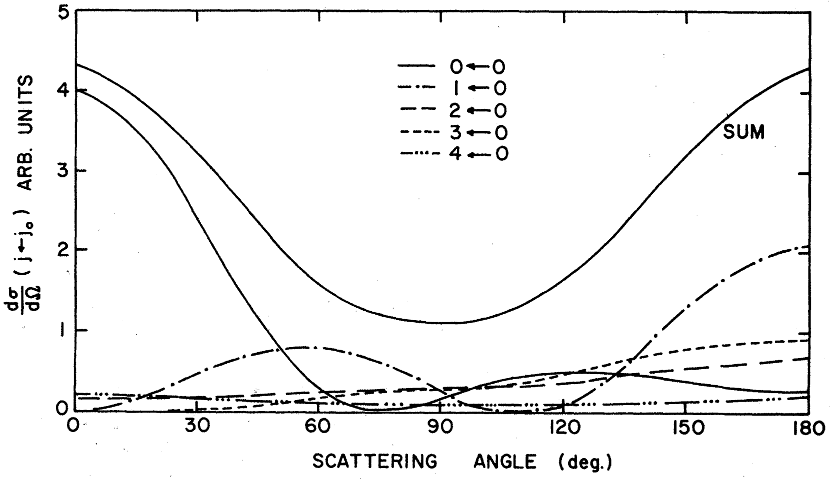

FIG. 2. Angular distributions for rotational-vibrational excitation of CO by electrons at 1.8 eV. The initial rotational state is taken to be $j = 0$.

TABLE I. Integrated rotational cross sections in CO computed with $\cos 2\beta = 0.25$. These values have the same normalization as the expression in the curly bracket of Eq. (5). Actual cross sections for $v=1$ at incident energy of 1.8 eV are found by multiplying by 0.9×10^{-16} cm^2. j_0 and j are the initial and final rotational states, and the last column is valid only for large values of j_0 and j.

j_0 \ j	0	1	2	3	4	$\|\Delta j\|$
0	0.63	0.59	0.30	0.38	0.13	0.70
1	0.19	0.71	0.54	0.24	0.22	0.35
2	0.06	0.32	0.72	0.44	0.19	0.13
3	0.05	0.10	0.31	0.71	0.41	0.12
4	0.01	0.07	0.10	0.32	0.70	0.04

nuclear molecule, $|\cos 2\beta|$ must be different from one, with a positive value favoring *p* character and a negative one *d*. In fact, the value of 0.25 for the CO resonance implies the *p*/*d* amplitudes are in the ratio 5 to 3. Therefore the parameter-free expression used by ELLT for the CO resonance is equivalent to the misleading assumption of Πu symmetry and would forbid the strong $|\Delta j| = 1$ rotational transitions. (See Table I.) More generally, we expect near-homonuclear (e.g., isotope-substituted homonuclear) molecules or covalent resonances to have $\cos^2\beta$ nearly one, hence having very small cross sections for $\Delta j =$ odd transitions. On the contrary, highly polar molecules or ionic resonances should have a value for $\cos^2 2\beta$ of nearly zero with $\Delta j =$ odd cross sections equal to those $\Delta j =$ even. Thus $\cos^2 2\beta$ may be regarded as a coefficient of covalency useful for classifying resonances of the same (cylindrical) symmetry.

Taking an experimental viewpoint, the theory developed here appears capable of working as a powerful microscope. From an inherently low resolution measurement (100 meV, characteristic of vibrational levels), one can reconstruct the whole rotational spectrum with its requisite high resolution of about 1 meV. Specifically, detailed cross-sectional information for which the rotational states are fully resolved is of great importance in the areas of interstellar molecules, and maser and laser spectroscopy.

Unfortunately, the prospect for a direct verification of this aspect of the present theory for CO seems remote at present, since the rotational constant is only 0.24 meV. However, in other molecules such as HF where the rotational constant is 2.6 meV, a direct measurement of some rotational-vibrational cross sections seems feasible. Application of the present theory to a $^2\Sigma^+$ resonance as in HF is discussed elsewhere.[6]

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[1] E. S. Chang, Phys. Rev. A 16, 1841 (1977), the preceding paper.

[2] T. F. O'Malley and H. S. Taylor, Phys. Rev. 176, 207 (1968). In Fig. 2 of this paper, it is shown that if one normalizes at 90°, the fit at 20° is off by a factor of 2, but if one normalizes at 60°, somewhat better agreement is found (with the worst being 40% off at 90°). The more general expression given by Eq. (28) appears to be equivalent to the results of Ref. 4.

[3] F. H. Read, J. Phys. B 1, 893 (1968); J. N. Bardsley and F. H. Read, Chem. Phys. Lett. 2, 333 (1968).

[4] H. Ehrhardt, L. Langhans, F. Linder, and H. S. Taylor, Phys. Rev. 173, 222 (1968).

[5] To facilitate comparison with formulae in ELLT, we use exact fractions here rather than decimals in Table I of I.

[6] E. S. Chang, J. Phys. B 10, L395 (1977).