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ELECTRON SCATTERING BY X^2gH_2 AT 10 eV
WITH EXCITATION OF NUCLEAR MOTION

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The cross sections for vibrational excitation of molecules (within the ground electronic state manifold) are larger than those predicted by considering the scattering of electrons in the static potential field of the unperturbed molecule. Larger excitation cross sections are predicted, however, by allowing for virtual excitation of excited electronic states (polarization) in the molecule¹ and/or temporary compound negative-ion formation.² In an attempt to understand these effects quantitatively we have performed the first electron-molecule calculations which simultaneously consider the static potential (including the long range quadrupole interaction), the polarization potential, and electron exchange effects. The calculations are performed in the Born (B) and Born-Ochkur-Rudge (BOR)³ approximations. We also report new experimental differential cross sections (DCS) for elastic and inelastic scattering. (The experi-

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mental techniques are discussed elsewhere.) The present calculations agree better with the experimental elastic DCS than any previous calculations.

In the Born approximation the scattering amplitude is calculated from the potential

$$V(\vec{r}, \vec{R}) = V_0^C(r, R) - \frac{\alpha(R)}{2r^4} g(r) + \left[V_2^C(r, R) - \frac{Q(R)}{2r^3} f(r) - \frac{\alpha'(R)}{2r^4} g'(r) \right] P_2(\hat{r} \cdot \hat{R}) \quad (1)$$

where $\vec{r}$ is the position of the scattering electron and $\vec{R}$ is the internuclear axis. V_0^C and V_2^C are the short range parts⁴ of the static potential which fall off as $r^{-1} \exp(-2Zr)$ at large r where Z is the effective nuclear charge;⁵ $Z(R) = 1.0 + 0.6875 \exp(-1.0002343 R)$. They are sums, integrated over orientation with Legendre polynomial weighting factors, of electron-nuclear attractions and electron-electron repulsions between the scattering electron and the two atoms. Q , α , and α' are the molecular electric quadrupole moment, the spatially averaged polarizability, and the anisotropic polarizability, respectively. The amplitudes for scattering off the five terms in the potential (1) will be denoted S_0 , P_0 , S_2 , Q_2 , and P_2 , respectively. The functions f , g , and g' are one for large r ; and $f = r^3/a_Q^3$ for $r < a_Q$. The input data set for the calculation specifies the value of the adjustable cutoff parameter a_Q and the forms of g and g' .

In the BOR approximation the effect of exchange is included in the Ochkur-Rudge approximation.⁶ Then the exchange amplitude E_0 is calculated from the electron-electron interaction part of V_0^C . In the B and BOR approximations the scattering by the symmetric and asymmetric components of the potential is independent. The differential cross section is then

$$\text{DCS}(\theta) = |S_0 + P_0 + E_0|^2 + |S_2 + Q_2 + P_2|^2. \quad (2)$$

The parameters for the calculations shown in Figs. 1 and 3 are specified by data set 1. These calculations use the D form (see Ref. 1) for g and g' with their parameters selected to give good agreement with the polarization potential calculated by Lane and Henry.⁷ This D polarization potential is much shallower than that usually used in semiempirical treatments; the depth of its spherically symmetric part and its coefficient of $P_2(\hat{r} \cdot \hat{R})$ are -0.091 and -0.039 hartrees, respectively. Further we select $a_Q = 2.0 a_0$ to give the best agreement of our static potential with the ab initio potential of Ardill and Davison.⁸ The calculated DCS using six or five (no exchange) of the amplitudes in Eq. (2) for vibrational excitation are shown in Fig. 1 as BOR and B, respectively. Also shown are the predicted DCS when only some of the interactions are included--these curves are labelled by the amplitudes retained in Eq. (2). Some previous workers thought that using only a polarization potential might not be too bad an approximation for predicting low energy integral cross

sections (the integral cross section is the integral of the DCS over all scattering angles). But Fig. 1 shows how important it is to keep all the interactions for a determination of large angle scattering.

Fig. 1 also shows the experimental differential cross section with a typical error bar (30%). This DCS is placed on an absolute scale by its measured ratio to the elastic DCS. The elastic and inelastic DCS are extrapolated to 0° and 180° , integrated, and normalized to the total scattering integral cross section ($32.1 a_0^2$) of Golden, Bandel, and Salerno.⁹ The integral cross section for vibrational excitation predicted by the experiment is then $0.28 a_0^2$. Ehrhardt et al.¹⁰ determined a DCS with the same shape as ours and estimated an integral cross section of $0.30 a_0^2$. Their DCS, normalized such that it is $(0.30/0.28)$ times ours at 40° , is also shown in Fig. 1. The integral cross sections predicted by the BOR and B approximations are 0.239 and $0.221 a_0^2$, respectively. [Using only the polarization potential ($P_0 P_2$ in Fig. 1) gives $0.109 a_0^2$ while neglecting the polarization potential ($S_0 E_0 S_0 Q_2$ in Fig. 1) gives $0.048 a_0^2$.] The agreement between the magnitude of the theoretical cross section (no arbitrary parameters) and the experimental one is better than we had a right to expect.

Fig. 2 is like Fig. 1, but it is from computations with another data set (called DS3). This potential is less justifiable a priori but gives slightly better agreement with the shape of the DCS. DS3 takes $a_Q = 1.7 a_0$ and g and g' in Model B¹ (r^4/a_P^4 for $r < a_P$) with the step a_P at $1.7 a_0$.

The depth of this polarization potential is -0.3100 hartrees for the spherically symmetric part and -0.0720 hartrees for the coefficient of $P_2(\hat{r} \cdot \hat{R})$. This calculation gives integral cross sections of 0.627 and $0.585 a_0^2$ in the BOR and B approximations. A deep polarization potential like this is believed to be inaccurate because of nonadiabaticity effects.^{11,7} In the calculation of integral cross sections such a potential is sometimes justified as compensating for neglect of exchange.¹² Fig. 2 also compares the scattering cross sections $|P_0|^2$ for data set 1 and DS3. This shows that the main difference in the two calculations is that scattering off the polarization potential which extends to the origin (the Model B potential) yields a DCS that decreases slower with scattering angle than does the polarization potential which is zero at the origin (the Model D potential). Thus the added potential does mimic exchange but of course only qualitatively. The discrepancy between theory and experiment at large scattering angles is probably a failure of our modified Born approximation treatment of the scattering or of the assumed R dependence of the polarization potential for small r [see Eq. (1)]. Otherwise, it would imply that the polarization potential of Lane and Henry is too shallow and that their assumption of complete "nonpenetration" is too severe.

Since our calculation gives cross sections large enough to account quantitatively for the $0 \rightarrow 1$ DCS at 10 eV without including resonance states, it casts doubt on any interpretation¹⁰ of this cross section mainly in terms of resonance contributions. Probably less than half the excit-

ation cross section at 10 eV is due to the resonance interaction. Our calculations for the $0 \rightarrow 2$ excitation, however, appear to be too small by one or two orders of magnitude and the excitation of this state is probably predominantly due to the resonance mechanism.

The short range central potential is more important for the elastic scattering than for the vibrational excitation. This is shown in Fig. 3 which compares the complete BOR calculation with experiment (normalized as discussed above). Also shown are the calculations which neglect exchange and/or polarization. These four calculations predict integral cross sections of 53.1, 31.1, 42.2 and $12.6 a_0^2$, respectively. The last two compare with integral cross sections of 34.4 and $20.4 a_0^2$ obtained by Wilkins and Taylor¹³ by solving the continuum Hartree-Fock equations numerically without a polarization potential and with and without exchange, respectively. Calculations which do not include the polarization cannot account for the shape of the DCS with its large forward peak. Finally, Fig. 3 also shows Born calculations which include only the polarizability (the scattering due to this is mostly in P_0 in this case) and only the asymmetric static interaction. These curves yield integral cross sections of 5.73 and $0.52 a_0^2$, respectively.

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Figure Captions

Figure 1. Theoretical DCS with data set 1 for vibrational excitation ($0 \rightarrow 1$) of H_2 at 10 eV impact energy. Also shown are the experimental cross sections determined in this work (crosses) and by Ehrhardt et al. (circles).

Figure 2. Theoretical DCS with DS3 for vibrational excitation ($0 \rightarrow 1$) of H_2 at 10 eV impact energy. Also shown is the cross section for scattering off the symmetric polarization term in the potential of data set 1.

Figure 3. Theoretical DCS with data set 1 for elastic scattering of electrons off H_2 at 10 eV. The experimental data, which is an average of three sets, is shown with 20% error bars in the range $8.5-78.5^\circ$.