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# Vibrational excitation of $H_2$ by electron impact: An energy-dependent vibrational-frame-transformation approach

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An energy-dependent rovibrational-frame-transformation method, combined with the multichannel quantum-defect theory, has been applied to study the vibrational excitations of $H_2$ by electron collision in the energy range below 5 eV. A class of nonadiabatic effects resulting from large collision time delay has been accounted for. Using a special set of short-range Born-Oppenheimer eigenstates, this approach does not explicitly introduce electron-molecule compound states. We show that the body-frame quantum-defect function $\mu_{l=1}(\varepsilon,R)$, containing the information about the dynamical coupling of the incident electron and the molecular target, is all one needs to describe the scattering properties of the system.

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It has been known for some time that the $H_2^-$ $(^2\Sigma_u^+)$ shape resonance at about 3-eV incident electron energy plays a dominant role in the vibrational excitation cross sections of $H_2$ by low-energy electron scattering (below 5 eV) [1,2]. Angular distribution measurements show that the scattering electron has mostly *p*-wave character [2]. This resonance state is short lived (having a decay width of several eV) at small internuclear distances $R$ and becomes a true bound state for $R>3$ a.u. Therefore there is no clear evidence of the existence of this resonant state in the elastic-scattering cross section (for electrons incident on the $v=0$ vibrational level), as this probes the small-$R$ region where the resonance is extremely broad. The study of rovibrational excitations and dissociative attachment, particularly from $v>0$ initial states, helps to probe the large-$R$ region where the resonance is long lived. Theoretical studies based both on resonance models [3–5] and on nonresonant descriptions [6–8], or on close coupling calculations [9,10], are present in the literature to describe this scattering process.

We present in this Brief Report a calculation of vibrational-excitation cross sections of $H_2$ by electron collision using an energy-dependent rovibrational-frame-transformation method [11] in conjunction with the multichannel quantum-defect theory (MQDT) [12,13]. As opposed to most other resonance treatments [2–5,14–16], this approach does not explicitly invoke an electron-molecule compound state. (The approaches of Nesbet [17] and Morrison [8] also do not introduce any compound states, but include the resonance effect—the strong energy dependence of short-range scattering parameters—in approximate ways.) Our short-range Born-Oppenheimer eigenstates are chosen in such a way that *the compound potential is the potential of the unperturbed molecular target.* All the dynamical coupling between the incident electron and the molecular target is included in the body-frame scattering phase phift [or quantum-defect function $\mu_{l=1}(\varepsilon,R)$] in the form of its energy dependence [18,11] (in addition to its $R$ dependence). This energy dependence is treated in our rovibrational frame transformation in a simple way.

We extend our previous vibrational-frame-transformation method [11] to include rotational excitations as well as more than one outer-electron partial wave. We consider a problem having a single electronic channel. Electronic excitations of the target have not yet been understood within our approach. Along the lines of MQDT, the configuration space of the scattering electron is divided into two regions: a reaction zone $(r\leq r_0)$ around the target and an asymptotic region $(r\geq r_0)$ far from the target. ($r_0$ is slightly larger in size than the molecular target and is usually several Bohr radii.) The complicated interactions between the scattering electron and the target, including exchange, polarization, and electronic correlation effects, are confined within the reaction zone. Due to the strong molecular field, the Born-Oppenheimer approximation is well justified in this region [19]. All that the short-range interaction does is to contribute a scattering phase shift (or quantum defect) to the solution in the asymptotic region. Once the scattering electron is outside the reaction zone, the time scale of its motion may become comparable to that of the nuclei. A laboratory-frame close-coupling expansion in terms of the complete eigenstates of the molecular target is more suitable in this region. The frame-transformation method of Chang and Fano [19,20] serves as a vehicle to connect the body-frame Born-Oppenheimer solutions in the reaction zone to the laboratory-frame close-coupling solutions in the asymptotic region. Body-frame scattering parameters are thus transformed into laboratory-frame scattering observables.

Our goal is to solve the Schrödinger equation, using the Born-Oppenheimer approximation inside the reaction zone only, at a given total energy $E$. Most theoretical treatments using compound states [2–5,14–16] first solve for the electronic eigenstates with some prescribed boundary conditions at the reaction-zone surface. Then the electronic eigenenergies serve as potentials along which the nuclei vibrate and rotate. Our approach starts from a different point of view. For scattering problems, the boundary values of the electronic wave functions are usually not known in advance since the scattering electron is in a continuum state (although the wave function of the $N$ target electrons is assumed to be negligible beyond $r_0$). This gives rise to a fundamental *arbitrariness* in specifying the fixed-nuclei energy of the compound. In other words, for a given total energy $E$, there is an infinite number of degenerate Born-Oppenheimer solutions within the reaction zone, each of which corresponds to a different choice of the boundary conditions on the electronic wave function.

We identify a *particularly simple and convenient class* of short-range Born-Oppenheimer eigenstates at total scattering energy $E$ from this infinite number of possible choices. The nuclear wave functions in this set are *required* to be those of the target nuclei, i.e., obeying the following nuclear Schrödinger equation:

$$\left[-\frac{1}{2\mu_N}\frac{d^2}{dR^2}+V_{\Lambda}^{(N+1)}(R)+\frac{J(J+1)-\Lambda^2}{2\mu_N R^2}-E\right]\chi(R)=0 . \tag{1}$$

We use a compound potential $V_{\Lambda}^{(N+1)}(R)$, which is the potential-energy curve of the molecular target $V_{\Lambda_0}^{(N)}(R)$ except for an $R$-independent constant $\varepsilon$,

$$V_{\Lambda}^{(N+1)}(R)=V_{\Lambda_0}^{(N)}(R)+\varepsilon . \tag{2}$$

Thus nuclear wave functions $\chi_{\Lambda J v}(R)$ and their corresponding energy eigenvalues $E_{\Lambda J v}$ are those of the molecular target except that they are solved with total angular momentum $J$ and total electronic angular momentum component $\Lambda$ along the internuclear axis. For each total energy $E$, $\varepsilon$ is quantized according to $\varepsilon_{\Lambda J v}=E-E_{\Lambda J v}$. Since $\varepsilon_{\Lambda J v}$ is $R$ independent, our compound potential-energy curves are parallel to that of the target. This class of Born-Oppenheimer eigenstates consists of a very special representation of the short-range compound states in which *the existence of the scattering electron does not alter the nuclear motion.*

When the electron moves just beyond the core (but is still within the Born-Oppenheimer region), these special Born-Oppenheimer eigenstates can be written as

$$\begin{aligned}\Psi_{l'\Lambda v}^{JM}=&\mathcal{A}\,\psi_{\Lambda_0}^{(e)}(N)\frac{\chi_{\Lambda J v}(R)}{R}r^{-1}\\&\times\sum_{l}X_{JM}^{(l\Lambda)}(\hat{r}',\hat{R})[f_{l\varepsilon_{\Lambda J v}}(r)c_{ll'}^{\Lambda}(\varepsilon_{\Lambda J v},R)\\&-g_{l\varepsilon_{\Lambda J v}}(r)s_{ll'}^{\Lambda}(\varepsilon_{\Lambda J v},R)],\quad r>r_0 .\end{aligned}\tag{3}$$

Here $\psi_{\Lambda_0}^{(e)}(N)$ is the target electronic state (for simplicity, we assume $\Lambda_0=0$, i.e., a $\sum$ target electronic state), $X_{JM}^{(l\Lambda)}(\hat{r}',\hat{R})$ is an eigenfunction of total angular momentum with $\hat{r}'$ denoting the radial coordinate of the outer electron in the body frame. $f_{l\varepsilon_{\Lambda J v}}$ and $g_{l\varepsilon_{\Lambda J v}}$ are regular and irregular radial solutions (evaluated at energy $\varepsilon_{\Lambda J v}$ and $l$) of the outer electron in the long-range field of the molecular target (which can be taken to be zero field for electron scattering by neutral species when polarization effects are negligible at $r>r_0$). $\mathcal{A}$ is the antisymmetrization operator. The $\mathbf{c}^{\Lambda}$ and $\mathbf{s}^{\Lambda}$ matrices contain all the information about the interaction between the incident electron and the target in the body frame, and can be obtained from *ab initio* calculations.

In the asymptotic region, the independent solution (3) can be written as a channel expansion in terms of the target eigenstates together with the outer electron's angular wave function

$$\begin{aligned}\Psi_{l'\Lambda v}^{JM}=&\mathcal{A}\,\psi_{\Lambda_0}^{(e)}(N)r^{-1}\sum_{l,N^+,v^+}\frac{\chi_{N^+v^+}(R)}{R}\Phi_{JM}^{(lN^+)}(\hat{r},\hat{R})\\&\times[f_{lN^+v^+}(r)I_{lN^+v^+,l'\Lambda v}\\&-g_{lN^+v^+}(r)J_{lN^+v^+,l'\Lambda v}],\quad r>r_0\end{aligned}\tag{4}$$

where the $\chi_{N^+v^+}(R)$ are the target nuclear eigenfunctions. $\Phi_{JM}^{(lN^+)}(\hat{r},\hat{R})$ is an eigenfunction of the total angular momentum operators of the system, and is related to $X_{JM}^{(l\Lambda)}$ through a unitary transformation [19]. The **I** and **J** matrices, containing all the scattering information required in the laboratory frame, are obtained by matching the above equation to the inner region solution, Eq. (3), at $r=r_0$. The rovibrational frame transformation matrices can thus be obtained as follows:

$$\begin{aligned}I_{lN^+v^+,l'\Lambda v}&\\=&\frac{\pi}{2}U_{N^+\Lambda}^{(lJ)}([f_{l'\varepsilon_{\Lambda J v}},g_{lN^+v^+}]C_{lN^+v^+,l'\Lambda v}\\&-[g_{l'\varepsilon_{\Lambda J v}},g_{lN^+v^+}]S_{lN^+v^+,l'\Lambda v}) ,\end{aligned}\tag{5a}$$

$$\begin{aligned}J_{lN^+v^+,l'\Lambda v}&\\=&\frac{\pi}{2}U_{N+\Lambda}^{(lJ)}([f_{l'\varepsilon_{\Lambda J v}},f_{lN^+v^+}]C_{lN^+v^+,l'\Lambda v}\\&-[g_{l'\varepsilon_{\Lambda J v}},f_{lN^+v^+}]S_{lN^+v^+,l'\Lambda v}) ,\end{aligned}\tag{5b}$$

where $[f,g]$ denotes a radial Wronskian evaluated at $r_0$.

Equation (5) consists of two parts. The rotational-frame transformation ($U_{N^+\Lambda}^{(lJ)}$) is simply a trivial geometrical transformation since it relates an angular momentum eigenstate relevant in the inner region (where $\Lambda$ is a good quantum number) to one relevant in the outer region (where $N^+$ is a good quantum number). The vibrational-frame transformation is accomplished by the following matrix elements of the short-range scattering parameters $c_{ll'}^{\Lambda}$ and $s_{ll'}^{\Lambda}$ between vibrational wave functions of the target:

$$C_{lN^+v^+,l'\Lambda v}=\int\chi_{N^+v^+}(R)c_{ll'}^{\Lambda}(\varepsilon_{\Lambda J v},R)\chi_{\Lambda J v}(R)dR , \tag{6a}$$

$$S_{lN^+v^+,l'\Lambda v}=\int\chi_{N^+v^+}(R)s_{ll'}^{\Lambda}(\varepsilon_{\Lambda J v},R)\chi_{\Lambda J v}(R)dR . \tag{6b}$$

It should be noted that both $\chi_{N^+v^+}(R)$ and $\chi_{\Lambda J v}(R)$ are evaluated in the same target potential $V_{\Lambda_0}^{(N)}(R)$. But $\chi_{N^+v^+}(R)$ is calculated with $J$ replaced by $N^+$ and $\Lambda$ by $\Lambda_0$. Finally the short-range reaction matrix can be formed as $\mathbf{K}=\mathbf{J}\mathbf{I}^{-1}$, which is used to calculate either scattering cross sections or bound spectra in the standard MQDT calculations [13,20,16].

If only one partial wave of the outer electron is dominant in the asymptotic region, then $\mathbf{c}^{\Lambda}$, for instance, reduces to a number

$$c^{\Lambda}(\varepsilon,R)=\mathcal{N}_{\Lambda}(\varepsilon,R)\cos[\pi\mu_{\Lambda}(\varepsilon,R)] \; , \tag{7}$$

where $\mu_{\Lambda}(\varepsilon,R)$ and $\mathcal{N}_{\Lambda}(\varepsilon,R)$ are the body-frame quantum-defect function and electronic normalization factor respectively. However, $\mathcal{N}_{\Lambda}(\varepsilon,R)$ is complicated to evaluate in some applications. One may get around this complication by using the $\zeta_{\Lambda}(\varepsilon,R)$ defect [$-\tan\pi\zeta_{\Lambda}(\varepsilon,R)$ is the logarithmic derivative of the electronic wave function]. This quantity is defined as a phase shift relative to an alternative base pair $(\bar{f},\bar{g})$ and is related to the quantum defect in a simple way [16]. The normalization factor $\mathcal{N}_{\Lambda}(\varepsilon,R)$ is then determined simply by $\mathcal{N}_{\Lambda}(\varepsilon_{v,}R)=(\partial\zeta_{\Lambda}/\partial\varepsilon)^{-1/2}|\varepsilon=\varepsilon_{v}$ [16]. For purely vibrational interactions, Eq. (5a), for instance, reduces to

$$I_{v^+v^{+\prime}}=[\bar{f}_{v^{+\prime}},g_{v^+}]C_{v^+v^{+\prime}}-[\bar{g}_{v^{+\prime}},g_{v^+}]S_{v^+v^{+\prime}}, \tag{8}$$

with

$$C_{v^+v^{+\prime}}=\int\chi_{v^+}(R)\mathcal{N}(\varepsilon_{v^{+\prime}},R)\times\cos[\pi\zeta(\varepsilon_{v^{+\prime}},R)]\chi_{v^{+\prime}}(R)dR \; . \tag{9}$$

A similar expression holds for $S_{v^+v^{+\prime}}$, except with cos replaced by sin.

Our calculation of $H_2$ vibrational excitation cross sections is based on an *ab initio* fixed-nuclei $l=l$ quantum-defect function $\mu(\varepsilon,R)$, calculated very recently by Robicheaux [4]. We utilize the $\zeta(\varepsilon,R)$-defect formulation here in order to avoid some analytical complications in evaluating the normalization factor in the electronic wave function. The reaction zone is chosen to be within the region $r<7$ a.u. The vibrational frame transformation can be carried out by evaluating the matrix elements in Eq. (9). A similar expression for $S_{v^+v^{+\prime}}$ can be obtained by replacing cos by sin. With these energy-dependent frame-transformation matrices, we may apply standard MQDT procedures to evaluate the final cross sections.

Figure 1 gives our results for vibrational excitations from the ground vibrational level to the first and the second excited levels. Overall, our results are in good agreement with those of Robicheaux [4] using a modified energy-dependent vibrational-frame transformation of Greene and Jungen [16]. For energies above 1.5 eV, the present results for $v=0$ to $v=1$ excitation agree with beam experiments [2] and with close-coupling calculations [10]. However, our results are in better agreement with swarm experiments [21] for energies below 1.5 eV. The reason for this apparently fortuitous agreement seems to derive from our neglect of *s*-wave scattering, and of the quadrupole contributions to the long-range interaction, which plays an important role in the threshold region. We show in Fig. 2 the dominant vibrational-

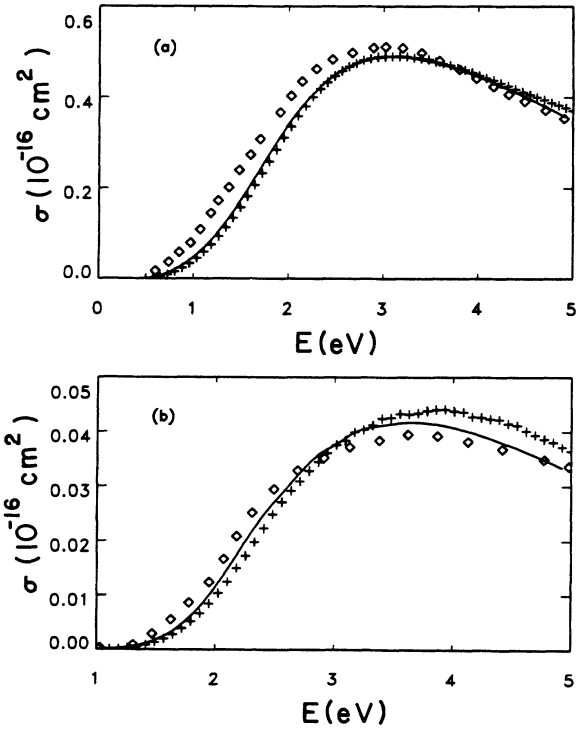

FIG. 1. Vibrational-excitation cross section from $v=0$ to (a) $v=1$ and (b) $v=2$ . Present results (+) are shown along with the calculation of Robicheaux (solid line) using a modified Greene-Jungen method [4]. Experimental results (◊) of Ehrhardt *et al.* are also shown [2].

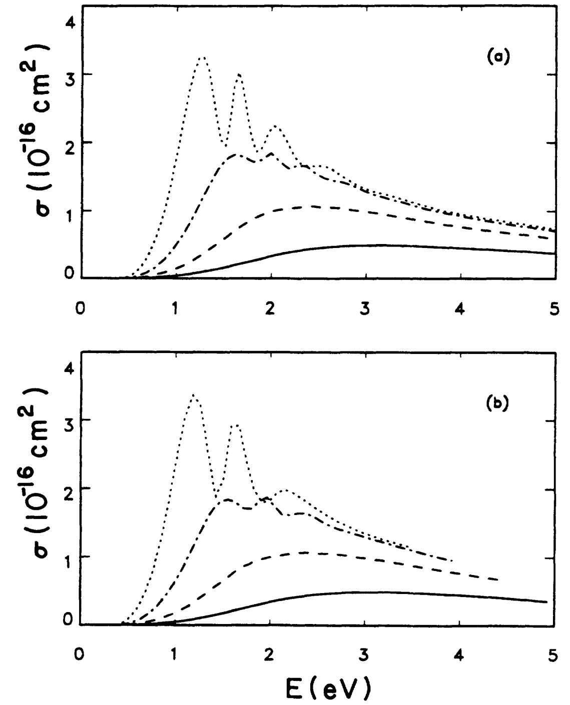

FIG. 2. Vibrational-excitation cross section in $e$-$H_2$ scattering, from $v=0$ to $v=1$ (solid lines), $v=1$ to $v=2$ (dashed lines), $v=2$ to $v=3$ (dash-dotted lines), and $v=3$ to $v=4$ (dotted lines). (a) Present calculation. (b) Results calculated by Robicheaux [4].

excitation cross sections for $v \rightarrow v+1$ starting from excited initial states $H_2(v)$. It is seen that the fine structures associated with vibrational levels of the negative ion state $^2\Sigma_u^+$ begin to emerge more clearly as $v$ increases. Since the resonance state is broader than the vibrational spacing for small internuclear distances, the resonant structures can hardly be seen for lower excitations. However, for higher excitations, the nuclei can be stretched into the region where the electronic resonance becomes long lived. For higher excitations ($v=3 \rightarrow v=4$, for instance), our results begin to differ from those of Robicheaux. Part of the reason for this is our neglect of the dissociation process in our calculation, i.e., we require the nuclear wave functions to vanish at $R_0=3.5$ a.u. As vibrational states (either initial or final) become higher, dissociative attachment will increasingly play a significant role.

In conclusion, our energy-dependent rovibrational-frame-transformation approach can be used to account for a class of nonadiabatic effects resulting from the energy dependence of the short-range scattering parameters. Without invoking electron-molecule compound states, we have calculated the vibrational excitation cross section of $H_2$ through the $H_2^-(^2\Sigma_u^+)$ shape resonance. It should be noted that our approach works equally well for calculating bound Rydberg spectra [22], since MQDT permits a unified treatment of continuum and bound states. Efforts to incorporate dissociative channels into this formulation are under way.

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