

Fingerprints of Broad Overlapping Resonances in the $e + \text{H}_2$ Cross Section

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We have shown here that the sharp peaks in the $e + \text{H}_2$ vibrational excitation cross section indicate the existence of transition states of H_2^- which have lifetimes 2–3 times larger than the lifetimes of individual overlapping H_2^- autoionization resonances. Each one of these transition states is associated with a collective ensemble of overlapping broad resonances of H_2^- and therefore does not necessarily decay exponentially in time. The structure in the experimental cross section is shown to be a result of the quantum interference between the overlapping resonances of H_2^- . [S0031-9007(98)07092-6]

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Sharp resonant structures in the energy dependence of vibrational excitation of H_2 by electron impact were predicted by theoretical calculations of Mündel *et al.* [1]. This structure appearing in the cross section for the excitations to higher vibrational levels of H_2 ($\nu \geq 2$) was experimentally confirmed by Allan [2]. The result was a surprising one since it is known that the $^2\Sigma_u^+$ resonance of H_2^- , responsible for the vibrational excitation in the low energy region is an extremely short-lived resonance with a lifetime comparable with the duration of the nonresonant scattering [3].

Domcke and Cederbaum proposed that vibrational degrees of freedom of H_2 are responsible for narrowing the width of the resonances of an intermediate state H_2^- [4]. However, to the best of our knowledge, no attempt was made to calculate the actual positions and widths of these resonances without the separation of electronic and vibrational motion.

The most usual method that allows the coupling between electronic and vibrational degrees of freedom of molecule is the Born-Oppenheimer (BO) approximation. Within the framework of this approximation electronic energy levels are found for fixed nuclei configuration. The electronic energy obtained as a function of nuclei distance serves later as a potential energy surface for vibrational motion of nuclei.

The BO approximation is applicable whenever the energy distance between the electronic states is larger than the coupling term between them. In such a case nuclei move on a single electronic potential surface, and the coupling to the others can be neglected. However, H_2^- intermediate for fixed internuclear distances $R < 3.2$ a.u. has no bound states. Because of the autoionization process it supports only continuum states. The distance between the electronic states of continuum is zero, hence the usual BO approximation would require dealing with an immense number of electronic potential surfaces strongly coupled with each other.

For a fixed H-H distance the H_2^- molecule decays exponentially with a rate depending on that distance. This exponential decay can be described by a single resonance

state possessing a *complex* electronic “energy.” The real part of the complex eigenvalue is the energy position of the resonance state, and the imaginary part is proportional to its decay rate (inverse lifetime). *From here it follows that instead of using many real coupled electronic potential surfaces within the BO approximation we can solve the nuclear Schrödinger equation with a single complex potential energy surface.*

In this Letter we will show that the sharp structures appearing in the vibrational excitation cross section despite the large width of the overlapping resonances are due to the interference effect between them. It is known that the structure in the cross section can be obtained if two overlapping resonances interfere with each other with desirable phases. The case of H_2^- is more complicated, and interference involves a large number of resonances. The key point, however, is the relatively large interaction of the discrete, vibrationally bound autoionization states of H_2^- with the slightly above the threshold states of H_2^- which are continuum states of nuclear motion but resonances because of the autoionization process.

In order to calculate the vibrational excitation cross section, σ_ν^L , we used the expression derived by Cederbaum and Domcke within the framework of the local complex potential approximation [5]:

$$\sigma_\nu^L(E) \propto \left(\frac{E - E_\nu}{E} \right)^{1/2} |\langle \nu | V_R(E - \hat{H})^{-1} V_R | 0 \rangle|^2. \quad (1)$$

This expression describes an incident electron of energy E hitting the H_2 molecule in its ground vibronic state and preparing the wave packet with entry amplitude $V_R|0\rangle$ on the potential energy surface of the H_2^- intermediate. The prepared wave packet is propagated via the nuclear Born-Oppenheimer H_2^- Hamiltonian \hat{H} with the complex potential,

$$\hat{H} = \hat{T}_N + V(R) - \frac{i}{2} \Gamma(R). \quad (2)$$

Finally, an electron with the energy of $E - E_\nu$ leaves the H_2 molecule in a vibrationally excited state. The

probability amplitude to obtain a specific vibrational state ν of H_2^- is determined by the exit amplitude $V_R|\nu\rangle$.

The scope of our work is to explain the existence of the structures in the vibrational excitation cross section rather than to obtain its correct numerical value. Therefore we will use a simplified expression for the cross section,

$$\sigma_\nu(E) = |\langle \nu | (E - \hat{H})^{-1} | 0 \rangle|^2. \quad (3)$$

The expression given above produces qualitatively the same structural phenomena as Eq. (1) does; however, it gives us a better physical insight into the problem.

Since our explanation of the phenomena is based on the vibrational eigenstates of the intermediate H_2^- we will use the spectral representation of the Green operator $(E - \hat{H})^{-1}$ in Eq. (3):

$$\sigma_\nu(E) = \left| \sum_\alpha \frac{\langle \nu | \alpha \rangle \langle \alpha | 0 \rangle}{E - E_\alpha} \right|^2, \quad (4)$$

where the sum is made over the vibrational eigenstates $|\alpha\rangle$ of the Hamiltonian defined in Eq. (2). E_α are the corresponding complex eigenvalues. $(\dots|\dots)$ is the generalization of the inner product for the non-Hermitian Hamiltonians [6]. The complex probability amplitude to populate the resonance state α is given by $\langle \alpha | 0 \rangle$, whereas the complex probability amplitude to decay from this resonance to a vibrational level ν is $\langle \nu | \alpha \rangle$. (On the complex probability amplitude see Ref. [7].)

In Fig. 1a we represent the energy levels of H_2^- when the autoionization process is neglected; i.e., $\Gamma(R) = 0$ in the Hamiltonian given in the Eq. (2). There are 9 infinite-lifetime vibrational bound states of H_2^- . In Fig. 1b we show the results obtained when the complex nonlocal Hamiltonian of H_2^- is diagonalized [i.e., $\Gamma(R) \neq 0$ in Eq. (2)]. The complex nonlocal potential, $V(R) - \frac{i}{2}\Gamma(R)$, was taken from Ref. [8]. As one can see when the imaginary part of the potential is taken into account, each vibrational state of H_2^- acquires a finite width. The vibrationally bound states become discrete resonance states, and the dissociative continuum now becomes a dissociative continuum of resonances. The discretization of the continuum is due to the usage of the finite basis set. The actual situation is of a branch cut. That is, a continuum of singular points of the scattering matrix.

Eigenstates of the H_2^- used in the calculation of the cross sections were obtained by diagonalization of the Hamiltonian matrix in the discrete variable representation (DVR) basis. Complex scaling (CS) of the H-H coordinate ($R \rightarrow Re^{i\theta}$) which is equivalent to the usage of absorbing boundary conditions in that coordinate was employed [9]. Application of CS enabled us to get rid of nonphysical weak oscillations in the cross section above the threshold energy to dissociation obtained in previous calculations [8]. We used only 200 grid points in the interval of 20 a.u., while the CS parameter $\theta = 0.25$ turned out to be the

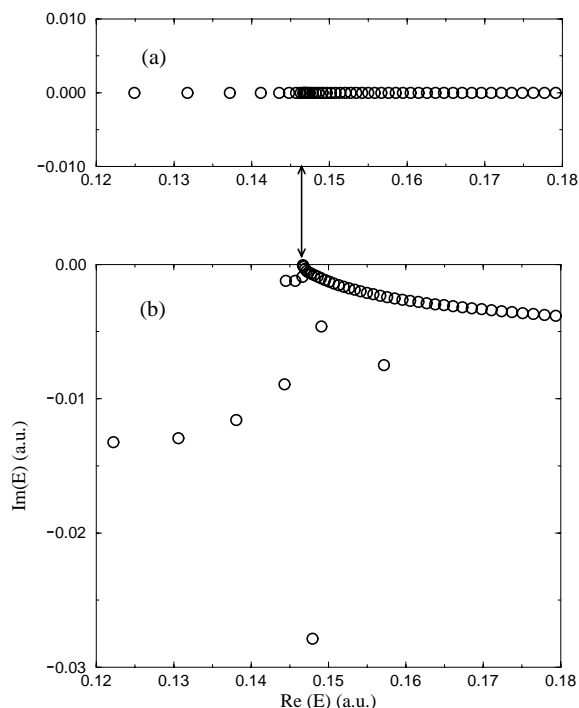


FIG. 1. The vibrational eigenstates of H_2^- obtained: (a) Ignoring the imaginary part of the potential, (b) with the full complex potential. The arrows stand for the threshold energy to dissociation at $E_{\text{threshold}} = 0.1467$ a.u.

optimal one for our calculations (resonance positions were insensitive to the variation of θ).

Cross sections for vibrational excitations $\nu = 0 \rightarrow \nu = 1, 2, \dots, 4$ calculated using Eq. (4) are represented in Fig. 2. The structures appearing under the dissociation threshold are in a good qualitative agreement with previous results obtained for the nonlocal theory [1,8]. Since the electronic resonance state of H_2^- decays by p waves, nonlocal effects will influence the scattering cross section, but not the quality of the interference effects due to nuclear dynamics. For discussion of local versus nonlocal effects see [5]. No structure is seen in the $\nu = 0 \rightarrow \nu = 1$ cross section. However, peaks below the dissociation threshold energy first appear for $\nu = 0 \rightarrow \nu = 2$ cross section and become even more pronounced for the excitations to higher vibrational levels.

The absence of the structure for the $\nu = 0 \rightarrow \nu = 0, 1$ excitation and formation of it for higher ones could suggest that the structure of the final state introduces the structure in the cross section. This effect is known as the reflection principle [10]. This possibility, however, was ruled out by the following numerical experiment. The cross section for the $\nu = 0 \rightarrow \nu = 0$ vibrational “excitation” was calculated, when the H_2^- Born-Oppenheimer potential was shifted in such a way that its minimum coincides with a minimum of the neutral H_2 molecule. *The shift affected only the shape of the broad background line leaving the fine structure in the cross section the same as obtained*

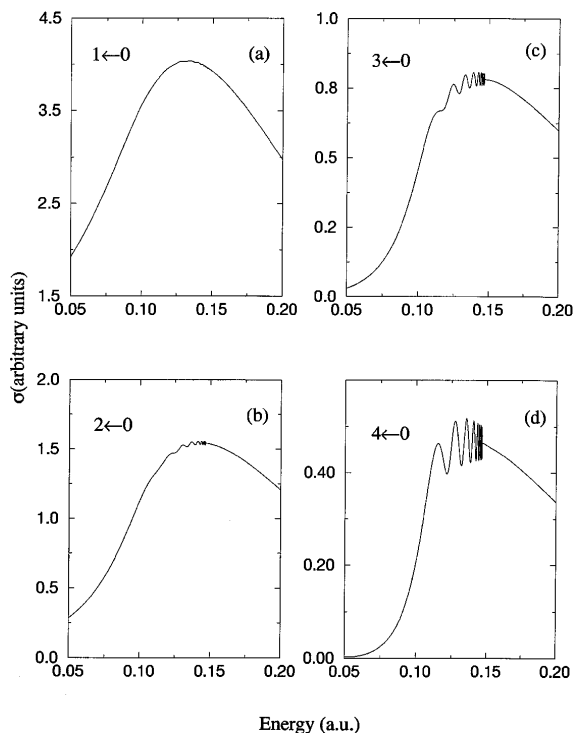


FIG. 2. Vibrational excitation cross sections $\nu = 0 \rightarrow \nu = 1, 2, \dots, 4$.

in Figs. 2b–2d. The conclusion is obvious: peaks in the cross section are unrelated to the structure of the initial or the final states and cannot be explained by the reflection principle.

Another possible explanation would be to relate the structure appearing in the vibrational excitation cross section to the discrete resonance states of H_2^- appearing at energies below the dissociation threshold energy. However, resonance positions do not coincide with the peak positions in the cross section. Moreover the widths of the peaks appearing in the cross section are 2 to 3 times smaller than the widths of the resonances calculated before. The structure appears in the cross section although the resonances are broad and overlapping. This effect can be achieved if the overlapping resonances interfere with each other with an appropriate phase. We have illustrated this phenomena for the case of two overlapping resonances following closely discussion given by Bohm [11].

Let us assume that $E_1 = \mathcal{E}_1 - \frac{i}{2}\Gamma_1$ and $E_2 = \mathcal{E}_2 - \frac{i}{2}\Gamma_2$ are two poles such that $\Gamma_1 = \Gamma_2 = \Gamma$, $\mathcal{E}_1 = 0$, and $\mathcal{E}_2 = \Delta E$. The cross section similar to Eq. (4) in the neighborhood of the poles is given by

$$\sigma(E) = \left| \frac{1}{E - \Delta E + \frac{i}{2}\Gamma} + \frac{C}{E + \frac{i}{2}\Gamma} \right|^2 \quad (5)$$

or

$$\sigma(E) = \sigma_1(E) + \sigma_2(E) + \sigma_{12}(E), \quad (6)$$

where $\sigma_1(E)$ and $\sigma_2(E)$ are the first and the second pole contributions to the cross section:

$$\sigma_1(E) = \frac{1}{E^2 + \Gamma^2/4}, \quad (7)$$

$$\sigma_2(E) = \frac{C^2}{(E - \Delta E)^2 + \Gamma^2/4}.$$

The last term in Eq. (6), $\sigma_{12}(E)$, stands for the interference effect between the two poles:

$$\sigma_{12}(E) = \frac{2CE(E - \Delta E) + 2C\Gamma^2/4}{(E^2 + \Gamma^2/4)[(E - \Delta E)^2 + \Gamma^2/4]}. \quad (8)$$

For $C = -1$ and for $\Delta E \leq \Gamma$ there is a single peak in the cross section at $E = \Delta E/2$. However, for $C = 1$ and $\Delta E = \Gamma$ the interference term $\sigma_{12}(E = \Delta E/2)$ gives a zero contribution to the cross section and consequently we obtain two well separated peaks in the cross section. As one can see, the widths of the peaks in $\sigma(E)$ are decreased due to the quantum interference effects. Following the Heisenberg uncertainty principle the uncertainty in energy times the lifetime of the system is larger than $\hbar/2$. Therefore we may say that by narrowing the widths of the peaks in $\sigma(E)$ one increases the lifetime of the system. Note that the usual concept of the lifetime as inverse of the decay rate is applicable only for isolated resonances and not in our case where there is a large overlap between the different resonances.

The same mechanism as described above introduces the structure below the threshold energy to dissociation in the case of H_2^- . Since the only states existing below this energy are the discrete resonances, one would expect that these states give the main contribution to the cross section below the threshold energy to dissociation. However, when the sum in Eq. (4) was truncated to include only the discrete resonances *no structure at all was obtained*.

The reason for that is the surprisingly large contribution of the continuum resonance states to the cross section. In Fig. 3 we present the population of the H_2^- states versus its energy positions.

One can clearly see that in addition to the large probability to populate the discrete resonance states, there is also a large probability to populate the continuum resonances at about 0.156 a.u. which are located slightly above the threshold to dissociation. If the imaginary part of the potential is ignored, the maximum in population of continuum states is located at different energy and is much smaller compared to the population of the discrete states. In order to explain this phenomena we plotted the wave functions of the continuum resonances corresponding to the maximum of population. It turned out that the amplitude of the wave function was two orders larger than the amplitude of the discrete resonance states. (Note that since the Hamiltonian is non-Hermitian the normalization of the wave functions is by the c product [6].) The

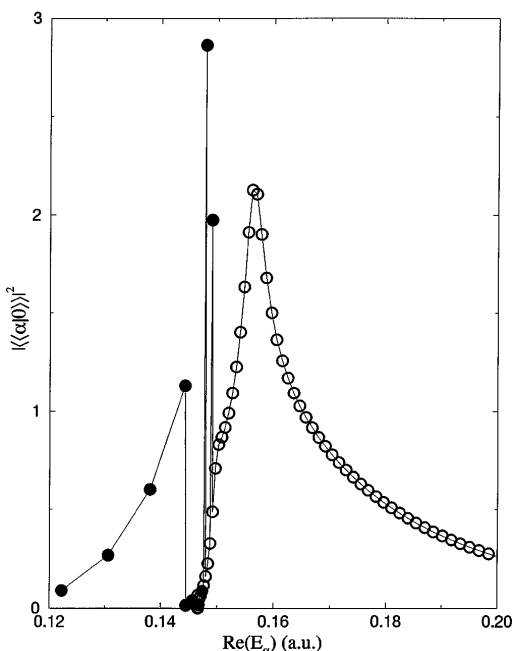


FIG. 3. Population of the H_2^- states by the initial wave packet. Filled circles represent the vibrationally discrete autoionization resonance states. Open circles represent the vibrational continuum of autoionization resonances.

unusually high amplitude of the continuum wave functions can be explained using the quasiclassical approximation. The quasiclassical continuum wave functions are of the form [12]

$$\Psi_{\text{continuum}}(R) = \frac{C_1}{\sqrt{p}} e^{i/\hbar \int p dR} + \frac{C_2}{\sqrt{p}} e^{-(i/\hbar) \int p dR}, \quad (9)$$

where $p(R) = \sqrt{2m\{E - [V(R) - \frac{1}{2}\Gamma(R)]\}}$. Since the potential in the case of H_2^- has a negative imaginary part, $\frac{1}{2}\Gamma(R)$, the momentum $p(R)$ acquires a positive imaginary component. Consequently, the second part of the expression given in Eq. (9) will be by some exponential factor larger than in the case of entirely real potential. Note that $\Gamma(R) \rightarrow 0$ as $R \rightarrow \infty$ and therefore $\Psi_{\text{continuum}}(R)$ does not diverge exponentially as in the case of vibrational predissociation resonances.

High amplitudes of the dissociative continuum autoionization resonance states wave functions lead to larger overlap of these states with the ground vibronic state of H_2 . The interference of the discrete resonance states with a continuum of autoionization resonances (i.e., branch cut of resonances) results in a sharp structure in the vibrational excitation cross section. The peaks obtained in the cross section are much narrower than the width of the individual resonance states, and their positions depend on the vibrational exit channel.

Assuming that the sharp peaks in the cross section *do not reflect the structure of the initial state* (as in the present case) we can associate the peaks with delay times in the propagation of the initial wave packet. On this ground we can say that we have shown that the sharp peaks in the $e + \text{H}_2$ vibrational excitation cross section indicates the existence of transition states of H_2^- which have lifetimes 2–3 times larger than the lifetimes of individual overlapping H_2^- autoionization resonances. Each one of these transition states (referred to as vibrationally resolved resonances in Ref. [13]) is associated with a collective ensemble of overlapping broad resonances of H_2^- and, therefore, does *not* necessarily decay exponentially in time. The sharp structure in the cross section and its dependence on the vibrational exit channel is obtained due to the quantum interference between the vibrationally bound autoionization states of H_2^- and the branch cut of dissociative continuum autoionization states of H_2^- .

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