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Cross sections for vibrational excitation of $\text{H}_2(X^1\Sigma_g^+, v'' = 0)$

via electronically excited singlet states populated by low energy electron impact

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Résumé. — Les sections efficaces d’excitation vibrationnelle de $\text{H}_2(X^1\Sigma_g^+, v'' = 0)$ après passage sur les niveaux électroniques singulets B, B', C et D et retombée radiative sur les différents niveaux vibrationnels de l’état fondamental sont calculées en fonction de l’énergie des électrons (0-150 eV) pouvant créer cette excitation indirecte. Des maxima apparaissent vers 50 eV et sont environ 20 à 40 % plus élevés que ceux obtenus par Hiskes en ne tenant compte que de l’excitation électronique des niveaux B et C.

Abstract. — Absolute cross sections are calculated for excitation of hydrogen, $\text{H}_2(X^1\Sigma_g^+, v'' = 0)$, on its different vibrational levels, by radiative decay from the B, B', C, and D electronic singlet states first populated by low energy electron collisions. The cross sections present a maximum around 50 electron-volts, but about 20 to 40 % higher than those reported by Hiskes considering the same excitation process only through the B and C electronic singlet states.

Electronic excitation of molecules by low energy electron impact is widely encountered among the interactions of various species in the upper atmosphere and is a fundamental process in gas laser physics, photochemistry, and chemical reaction dynamics. For example, in the ultraviolet hydrogen laser, electronic excitation by electron impact leads to population inversions between rovibrational levels of the electronically excited states and those of the ground state for which the probability of direct excitation is low. In our laboratory, these excited states $\text{H}_2(X^1\Sigma_g^+, v'')$ are also produced via electronically excited states of $\text{H}_2$ for studying the reactive scattering $\text{H}_2/\text{O}(^1\text{D}, ^3\text{P})$ in a crossed beam experiment. In such a study, it is of great interest to open electronically excited channels, but the kinetic energy available in the centre of mass system is often well below the threshold of these reactive channels [1]. For instance an energy of 2.4 eV is needed to achieve the channel $\text{O}(^1\text{D}) + \text{H}_2$ ($v'' = 0$) → $\text{OH}(^2\Sigma^-) + \text{H}$. An interesting way for providing the system with this missing energy, can be found through the vibrational excitation of $\text{H}_2$ which is very efficient due to the relatively large energy gaps ($\lesssim 0.5$ eV) in this light molecule. This vibrational excitation is not attainable directly by laser light absorption because the molecule has no electric dipole moment between two $v$ states in the same electronic state. A direct excitation of the rovibrational states of $\text{H}_2(X^1\Sigma_g^+)$ could be obtained by collisions with molecules, ions, or slow electrons, but these processes are rather difficult to use and the cross sections are low. On the contrary, the excitation process by radiative decays from higher electronically excited states, is much more simple and efficient in particular for our reactive scattering experiment.

Laser absorption can be used for the first step of the process leading to electronic excitation of $\text{H}_2$. Nevertheless, the energy necessary (i.e. around 13 eV, or 100 nm, for reaching the B or C states) is not available without using the vacuum ultraviolet or the multiphoton techniques not yet sufficiently developed for operating easily in this energy range. On the other hand, low energy (20-300 eV) electron collisional excitation is a simple and much more efficient method, but with a rather poor selectivity. In fact, ionization, dissociation, and excitation on a number of electronic states, are produced simultaneously. As far as the hydrogen molecules undergo only a single collision
with the electrons and the ion-electron interactions can be neglected, the three dominant processes are:

\[ H_2 + e \rightarrow H + H + e \]  \hspace{1cm} (1)

\[ H_2 + e \rightarrow H_2^+ + 2 e \]  \hspace{1cm} (2)

\[ H_2 + e \rightarrow H_2(v^r) + e. \] \hspace{1cm} (3)

The respective cross sections are reported in figure 1 in terms of the incident electron energy [2-4]. It appears that the cross section corresponding to the dissociation process is strongly peaked around an electron energy of 20 eV and may be neglected for energies higher than 30 eV, in particular at 50 eV where the vibrational excitation becomes maximum. The ionization is the most efficient process at any energy but the ions formed can be easily removed from a molecular beam used in a crossed beam experiment. In spite of these competing phenomena, the ease of producing a relatively intense low energy electron beam stimulated us to investigate in detail its possibilities in vibrational excitation of \( H_2(X \, ^1\Sigma_g^+) \) in a supersonic molecular beam. Unfortunately, this procedure cannot be selective in populating the rovibrational states, even if the electronic excitation was obtained selectively. As a matter of fact, each final rovibrational level is populated by radiative decay from all internal levels of the upper electronic singlet states, according to the Franck-Condon principle. The experimental analysis of these populations will be made after developing VUV or multiphoton techniques. The results presented in this paper concern only theoretical predictions.

The present calculation leads to cross sections for excitation on individual vibrational states of the electronic ground state of \( H_2(X \, ^1\Sigma_g^+) \). Generally, electron excitation collisions populate both the triplet and the singlet states of the molecule. The triplet states can be ignored here because radiative decay towards the singlet ground state is not allowed. However, all the singlet states \( B, B', B'' \), \( D, D', E, F \) (and also the upper levels of the same \( g \) symmetry as \( E, F \) state) should be taken into account. The molecules on singlet levels of \( g \) symmetry decay to the ground state via a cascade procedure of the type \( E, F(g) \rightarrow B(u) \rightarrow X(g) \).

According to experimental data from Ajello and coworkers [4], it appears that this contribution to the \( B \) state population amounts to 10-20% of the number of molecules directly excited to the \( B \) state, for electron energy around 100 eV. This process is not considered in the following calculation, keeping in mind that the \( B \) state population is then underestimated of about 10 to 20%, this error being afterwards « scattered » on the populations of the different vibrational levels of the ground state. After the same authors [4], the cascade procedure through the \( C \) state can be neglected. The excitation cross sections on \( B' \) and \( D' \) states are negligible as compared to those of the other singlet \( u \) states [5]. In consequence, only the \( B, B', C \) and \( D \) states are included in the calculations with an overall underestimation within 10%. A similar calculation was made previously by Hiskes [6] who considered only the \( B \, ^1\Sigma_u^+ \) and \( C \, ^1\Pi_u \) levels as intermediate electronic states excited by the electrons. Thanks to very recent data from M. Glass-Maujean [7], it has been possible to include the states \( B \, ^1\Sigma_u^+ \) and \( C \, ^1\Pi_u \) and also \( B' \, ^1\Sigma_u^+ \) and \( D \, ^1\Pi_u \) in our treatment. The \( H_2 \) molecule is assumed to be initially in the vibrational state \( v'' = 0 \) of \( X \, ^1\Sigma_g^+ \) with a good approximation in a wide temperature range.

The rotational excitation is disregarded by using the simplification \( J' = J'' = 0 \) throughout the calculation. This seems to be reasonably realistic since the oscillator strengths are little affected by the variation of the initial rotational state, as shown [8] at least for \( J'' < 5 \) and \( v'' = 0 \). Such initial internal states are those encountered in the electronic excitation process, with a rotationally cooled medium as obtained in a supersonic molecular beam.

As an example, the excitation transition

\[ X, v'' = 0 \rightarrow B, v' \]

is now considered. The oscillator strength of the transition is proportional to:

\[ P(X, v'' = 0; B, v') = \left| \langle \chi(B, v', R) | D(R) | \chi(X, v'' = 0, R) \rangle \right|^2 \] \hspace{1cm} (4)
where the $\chi$'s are the vibrational wave functions of the initial and final states and $D(R)$ is the corresponding electronic dipole transition moment. If $\sigma(X \rightarrow B)$ is the cross section for the overall electronic excitation induced by electron collision, without any discrimination on the vibrational states, the cross section for excitation from $X$, $v'' = 0$ to $B$, $v'$ can then be written:

$$\sigma(X, v'' = 0; B, v') = \sigma(X \rightarrow B) \, P(X, v'' = 0; B, v')$$

in the framework of the Born approximation. Assuming the dipole moment $D(R)$ as independent of the internuclear distance $R$, in the range of interest, has little effect on the oscillator strengths [8]. Thus, it can then be factorized out of expression (4). The remaining Franck-Condon factor is equal to the fractional population in level $v'$ resulting from the electron collision. The decay transition is then considered

$$B, v' \rightarrow X, v'' .$$

If $A(v', v'')$ is the corresponding transition probability, the fraction of molecules finally in a given state $v''$ among the bound states is

$$\frac{A(v', v'')}{\sum_{v''} A(v', v'')} .$$

Each decay of a $(B, v')$ state does not lead to a bound state. This is taken into account in normalizing the preceding fraction by the sum of the Franck-Condon factors over the bound levels $v''$

$$b(v') = \sum_{v''} q_{v''} .$$

and

$$q_{v''} = \left| \langle \chi(B, v', R) \mid \chi(X, v'', R) \rangle \right|^2 .$$

Therefore the cross section for populating the level $X$, $v''$ via the level $B$ is

$$\sigma(B, v'') = \sigma(X \rightarrow B) \sum_{v'} P(X, v'' = 0; B, v') \times$$

$$b(v') \frac{A(v', v'')}{\sum_{v'} A(v', v'')} .$$

The total cross section for populating the level $(X, v'')$, by transitions through the $B, B', C$ and $D$ singlet states, is then:

$$\sigma(v'') = \sigma(B, v'') + \sigma(B', v'') + \sigma(C, v'') + \sigma(D, v'') .$$

The total cross sections for each electronic singlet state are taken from the work of Arrighini and coworkers [9]. Finally, the $\sigma(v'')$ cross sections for the different vibrational levels are shown in figure 2 in terms of the electron energy. The different curves exhibit the same shape with a maximum between 40 and 60 eV. At a given impact energy, the cross sections decrease monotonically with increasing $v''$. Nevertheless, a plateau is observed between about $v'' = 2$ and $v'' = 5$ (see Fig. 3). These results can be compared to those reported by Hiskes [6]. It appears then that neglecting transitions $X \rightarrow B''$ and $X \rightarrow D$ leads to an overall underestimation of about 30%, but the cross sections present nearly the same variations in terms of the electron energy. Nevertheless, the slope of $d\sigma/dE$ at low energy, close to the threshold, appears much larger in Hiskes' results [6] than in the present ones. This difference can be explained by the fact that the cross sections used by us for the electronic excitation processes [9], are slightly different from those used by Hiskes [6] and exhibit a plateau with a very steep decrease at the threshold. Also, the relative values for different vibrational levels are similar but the population inversion between the levels 12 and 13, as obtained by Hiskes [6], is not observed in the present results.
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References


Fig. 3. — Absolute cross sections versus final vibrational state at an electron energy of 60 eV.