

Vibrational dependence of negative-ion formation by dissociative attachment of low-energy electrons

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The vibrational dependence of dissociative attachment in low-energy $\text{Na}_2(v'') + e^-$ collisions ($E_{el} < 1.0$ eV) is studied with a crossed-beam apparatus. The Na_2 vibrational distribution is controlled through Franck-Condon pumping. A range of vibrational levels with energies up to approximately 60% of the molecular binding energy is covered. We observe a three orders of magnitude increase in the dissociative attachment rate for low lying and intermediate vibrational levels v'' . Further analysis shows a strikingly abrupt leveling off above $v'' \approx 12$.

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Characterizing the effects of internal nuclear motion on molecular scattering has recently emerged as an important line of inquiry in atomic and molecular physics. Vibrational excitation, for example, may play a crucial role in combustion, atmospheric, and plasmas processes. Excited nuclear motion increases the likelihood of deviation from Born-Oppenheimer behavior; accurate treatment of such phenomena is still a major theoretical challenge [1]. We study the influence of vibrational motion on the process of dissociative attachment (DA) of electrons to diatomic molecules. The DA cross section is remarkably sensitive to vibrational excitation [2–7], and can vary by several orders of magnitude. Aside from its fundamental importance, research concerning the vibrational dependence of DA is motivated by the recognition that neutral beam heating of controlled fusion plasma may benefit from elevated negative ion production rates associated with DA from vibrationally excited molecules, and in particular, from H_2 [8]. More recently, plasmas have been applied to the design of microelectronic devices; DA can be an important mechanism for controlling electron densities in such plasmas, and the knowledge of how vibrational excitation influences electron densities may become vital in the tailoring of plasmas to this and other applications [9]. Furthermore, electron-induced chemistry on surfaces is also concerned with transient formation of negative ions and the coupling of electronic and nuclear motion [10].

In this Rapid Communication, we present results from an experimental study investigating the vibrational dependence of the DA process which covers a large range of vibrational levels with internal energy up to approximately 60% of the molecular dissociation energy. In particular, we demonstrate for Na_2 that the DA rate rises by over three orders of magnitude for vibrational levels below the vicinity where the process is believed to become exoergic, while above the exoergic limit the DA rate is strikingly insensitive to further increases in the vibrational energy. The electronic structure of Na_2 is analogous to that of H_2 , D_2 , and Li_2 ; thereby allowing us to qualitatively compare our work to previous studies of the latter three species [2–5, 7].

In general, DA of diatomic molecules can be treated from the viewpoint of the resonance model [11,12]. Given that energy constraints are satisfied, the scattering of an electron by a diatomic molecule AB in its ground electronic state has the possibility of forming the resonance state AB^- with sufficient energy to dissociate (see Fig. 1). Assuming that the Born-Oppenheimer approximation is justified, an electron can be captured at $R_c(E_{el})$, the internuclear separation where the electron's kinetic energy E_{el} is equal to the vertical difference between the AB and the AB^- potential curves. Autodetachment is possible while the resonance state evolves toward the stabilization radius R_s , i.e., where the AB and the AB^- potentials intersect. The DA cross section therefore depends on the cross section for electron capture and on the width of the resonance state. Theoretical work [3] suggests that vibrational excitation influences the DA cross section by increasing the energy range over which electron attachment can occur, as well as by making electron capture closer to R_s possible and thereby increasing the negative ion's survival probability. The DA cross section for H_2 and D_2 , for instance, increases by several orders of magnitude over the lowest four or five vibrational levels [2]. Theoretical work suggests that the DA cross section should reach its maximum value in the vicinity where the vibrational excitation exceeds the

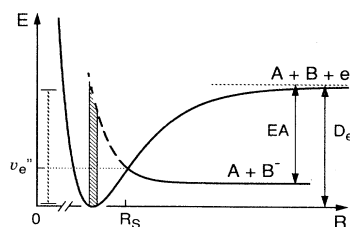


FIG. 1. Schematic potential of a molecule and its negative ion resonance state. For the $\text{Na}_2 X^1\Sigma_g^+$ potential D_e is 0.747 eV [13]. The electron affinity (EA) of Na is 0.548 eV [14]. The two curves cross at R_s , and the vertical dashed line indicates the width of the electron energy distribution.

exoergic limit, i.e., the potential energy at the stabilization radius [3, 4, 7].

Experimentally, several methods have been employed to produce vibrationally excited samples for DA studies. Recombination of hydrogen atoms on surfaces has been used to create vibrationally excited H₂ molecules [15], as has electron impact excitation [16]. Laser-based studies using a fixed frequency laser [17] and an infrared laser [18] have also been reported. Yet thermal excitation has been the predominant experimental method for preparing vibrationally excited distributions in diatomics [2, 19] and polyatomics [20]. All of these studies have found varying degrees of enhancement in the DA rate as a function of sample temperature. Although experimentally simple, thermal excitation is severely limited in the range of excited states that are accessible; furthermore, thermal excitation also changes the rotational level population. To circumvent these limitations, laser-based Franck-Condon pumping (FCP) [21] has been used to study DA in Li₂ [22]. The latter authors conclude that the DA rate varies little in the exoergic region. However, interpretation of their results is plagued by the existence of a substantial Li⁻ background. The resulting lack of sensitivity to Li⁻ originating from low vibrational levels prevents them from observing any significant increase in the DA rate as a function of vibrational excitation. Finally, we note that the absolute cross section for DA of Na₂ has previously been estimated through effusive beam experiments [23], but with no attempt to control the vibrational distribution. These authors conclude that the observed rate of negative ion production was dominated by population in vibrationally excited states; however, the cross section they reported is an average over cross sections that vary by approximately three orders of magnitude.

EXPERIMENT

We apply FCP of Na₂ to cover a large range of vibrational levels v'' and to systematically vary the v'' population distribution. The DA rate from excited vibrational levels is measured relative to the DA rate of the ground vibrational state. Negative ions produced through DA in a crossed-molecule-electron beam apparatus are recorded with time-of-flight ion detection. The molecular beam source, the laser excitation region, and the scattering region are each contained in separate, differentially pumped vacuum chambers. The source is typically operated at 900 K with the nozzle held 50 K hotter. The corresponding sodium vapor pressure of about 50 mbar results in a Na₂ molefraction in the molecular beam of 0.10 to 0.15 [24] with 99% of the Na₂ population in the ground vibrational state. For $v'' = 0$, the rotational distribution corresponds to a temperature of 27 ± 1 K for $j'' < 14$ and 43 ± 4 K for $j'' > 14$, as measured by laser-induced fluorescence. The $j'' = 9$ state carries 8.0% of the $v'' = 0$ population.

After collimation, the molecular beam passes into an intermediate chamber where Na₂ is prepared in vibrationally excited states via Franck-Condon pumping with single-mode dye lasers. The pump laser frequency is tuned to a $A^1\Sigma_u^+(v', j' = 10) \leftarrow X^1\Sigma_g^+(v'' = 0, j'' = 9)$

transition. Subsequent radiative decay populates a distribution of v'' levels with $j'' = 9$ and 11. The pump laser is tuned to various v' transitions, each one leading to a different v'' distribution, and thus a different mean level \bar{v}'' . Care is taken to saturate the pump transitions, i.e., to remove > 99% of the population from the ($v'' = 0, j'' = 9$) level. The ultimate vibrational distribution is governed by the relative transition probabilities and is proportional to $|\langle v'', j'' | v', j' \rangle|^2 \nu^3$ (the product of the Franck-Condon factor and the emitted photon frequency cubed). Upon inclusion of the dependence of the transition dipole moment on internuclear distance [25], the change in the population of any given level is less than 10%.

Following FCP, the molecular beam passes into the scattering chamber where it is crossed by a pulsed, magnetically guided electron beam with an energy resolution of 0.7 eV full width at half maximum. This source is based on the design of Ref. [26]. The electron beam is pulsed for 0.1–1.0 μ s. After an additional 0.1–0.2 μ s delay to allow electrons to escape from of the scattering region, a 1.0- μ s, 100-V pulse draws negative ions into a time-of-flight (TOF) mass spectrometer [27] with a resolution of better than 1 at 23 amu. The TOF is designed to allow for rapid polarity switching so that negative and positive ion signals can be compared.

We calibrate our collisional energy either by observing O⁻-CO₂ resonances [28] from a beam generated by introducing CO₂ into the unheated beam source, or by switching the TOF to the positive ion mode and measuring the threshold for collisional ionization of Na₂. Both methods give consistent results. The TOF is then set to the negative ion mode, and the electron energy is tuned close to zero. Since, at present, the energy width of our electron beam greatly exceeds the mean vibrational energy (see Fig. 1) and is broad when compared to the expected width of the DA resonance [23], a precise calibration of the collisional energy is neither possible nor necessary.

Data are collected by pulse counting at the Na⁻ flight time. The signals from vibrationally excited molecules, unexcited molecules (pump laser blocked), and the background (molecular beam blocked) are each measured for 10 s. This cycle is repeated 50–100 times per data point.

RESULTS AND DISCUSSION

Figure 2 shows typical TOF spectra for the three experimental cases. The diamonds represent data for $\bar{v}'' = 10.8$ (corresponding to $v' = 6$), while the inset shows both the background and the signal from unexcited molecules on an expanded vertical scale; these data demonstrate the large degree of enhancement of the DA rate that is realizable through vibrational excitation. A quantitative value of the DA enhancement is determined by taking the ratio of the signals for excited and unexcited molecules after having subtracted the background. Figure 3 shows the enhancement of the Na⁻ formation rate as a function of \bar{v}'' with the 8.0% pumping efficiency taken into account. The statistical error bars are approximately $\pm 5\%$ (three times the standard deviation). The

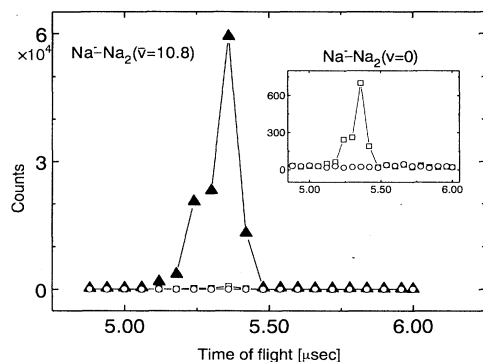


FIG. 2. Time-of-flight spectra for $v'' = 0$ (\square), $\bar{v}'' = 10$ (\blacktriangle), and background (\circ). The inset shows the $v'' = 0$ and the background spectra on an expanded vertical scale.

data presented in Fig. 3 show a sharp increase of the DA rate at low \bar{v}'' followed by a leveling off at high \bar{v}'' . The inset of Fig. 3 shows a typical v'' distribution. We have analyzed these data based on three simple assessments of the DA rate, $k(v'')$, as a function of v'' . We assume that $k(v'')$ rises from k_0 at $v'' = 0$ to k_{max} at a critical level v''_c ; the functional form of this rise, $f(k(v''))$, is taken to be either a step function, a linear function, or an exponential. Beyond v''_c , $k(v'')$ remains constant at k_{max} . These assumptions are motivated by theoretical work on electronically similar diatomic molecules [3, 4, 7]. We can express the enhancement, $E(\bar{v}'')$, as

$$E(\bar{v}'') = \left[\sum_{v''=0}^n f(k(v'')) \rho_{v'}(v'') \right] / k_0, \quad (1)$$

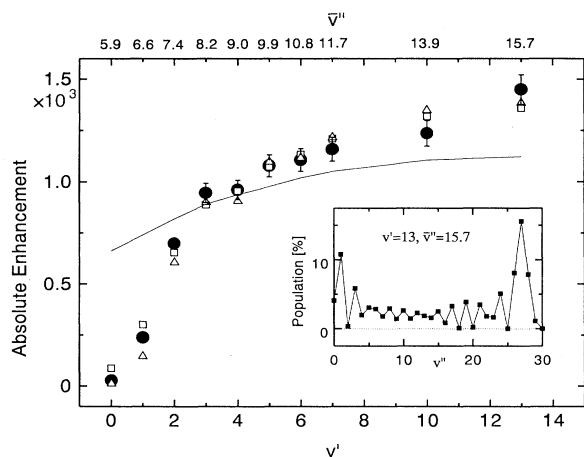


FIG. 3. Measured enhancement of the DA rate (\bullet) as a function of the average vibrational state \bar{v}'' (upper scale). The lower scale shows the $A^1\Sigma_g^+(v')$ state through which each $X^1\Sigma_g^+(v'')$ vibrational distribution is prepared. The left-hand scale shows the enhancement with the pumping efficiency (8.0%) taken into account. The inset shows a population distribution characterized by $\bar{v}'' = 15.7$. Also shown are the results of our data analysis assuming a functional dependence of $k(v'')$ that corresponds to a step function (\triangle), an exponential (\square), and a linear function (solid line).

where the summation is over all occupied v'' levels, and $\rho_{v'}(v'')$ is the v'' distribution that results from FCP through an individual v' level. The maximum enhancement, k_{max}/k_0 , and v''_c become free parameters here. A least squares fit of Eq. (1) to the experimental data of Fig. 3 yields the best values for v''_c and k_{max}/k_0 . The solid line of Fig. 3 shows that the linear function does not reproduce the experimental data well. The step function and the exponential, however, do furnish reasonably fits; the latter giving a slightly better result. The best fit occurs, for the step function, at $v_c = 12$ and $k_{max}/k_0 = 2.4 \times 10^3$, and for the exponential, at $v_c = 12.5$ and $k_{max}/k_0 = 2.2 \times 10^3$. Upon including the variation of the dipole transition moment when calculating the vibrational populations due to FCP, we find no change in v''_c and a 10% lowering of k_{max}/k_0 . This analysis establishes the crossing of the $\text{Na}_2(X^1\Sigma_g^+)$ and $\text{Na}_2^-(A^2\Sigma_g^+)$ potentials to be in the vicinity of $v'' = 12$; this is in good agreement with the *ab initio* calculations of Sunil and Jordan [29] which predict a crossing in the range $10 \leq v'' \leq 14$.

An estimate for the absolute DA cross section is furnished by the results from our data analysis in combination with the energy integrated cross section from Ref. [23]. The vibrational distribution of Ref. [23] corresponds to a temperature of 650 K. The energy integrated cross section for $v'' \geq v''_c$ should be, within a factor of 2, $7 \times 10^{-17} \text{ cm}^2 \text{ eV}$, and more than three orders of magnitude lower for $v'' = 0$.

Because of the strong increase of the DA cross section with v'' , the small population in $v'' = 1$ before FCP (on the order of 1% of the total population) may contribute as much as 10% to the negative ion signal without laser excitation. This factor would slightly reduce the apparent DA enhancement. Whereas this effect may be significant when comparing our results quantitatively to future related theoretical studies, it in no way changes our general conclusions.

In summary, we have presented data on the vibrational level dependence of the dissociative attachment rate covering a large range of vibrational levels up to $v'' \approx 28$ (see inset of Fig. 3). A simple analysis of the data supports theoretical predictions that the DA rate rises dramatically until the exoergic limit is reached (in the vicinity of $v'' = 12$), above which the DA rate shows strikingly little increase with v'' .

Future work will take this experiment a significant step forward by using the recently developed technique of coherent population transfer [30] for efficient and selective preparation of *individual* rovibronic states. This approach will also put us into position to study experimentally the vibrational dependence of the competing autodetachment channel leading to vibrational excitation. Furthermore, the use of resonantly enhanced two-photon ionization of atomic sodium using lasers to produce electrons with narrow energy resolution [31] should eventually allow the investigation of the electron energy dependence of these processes out of individual quantum states, and may prove crucial for identifying nonlocal effects in the DA process [32].

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