Vibrational effect on charge-transfer processes in collisions of H⁺ and O⁺ ions with C₂H₄ molecules at energies below 10 keV/u

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Charge-transfer processes in collisions of H^+ and O^+ ions with C_2H_4 molecules have been studied in joint theoretical and experimental approaches for collision energies below 10 keV/u. Since H and O atoms possess nearly identical ionization potentials, these two ions are expected to share similar dynamics and hence to have similar cross-section values for charge transfer, at least for the energy region above 100 eV. In the present experiments, these cross sections of H^+ and O^+ ions have been derived by the initial growth rate method in the energy range of 0.20 to 3.6 keV, while the present theoretical study has been carried out for H^+ impact only. We have examined the vibrational effect on charge transfer, especially the "temperature effect" of the initial vibrational states of the C_2H_4 molecule as well as the final vibrational states of the product $C_2H_4^+$ molecular ion. Indeed, a strong influence of the initial vibrational states on charge transfer has been observed since these vibrationally excited initial and final states force the process to be more nearly resonant, thus making charge transfer more efficient. This vibrational effect, and perhaps rotational effect as well, that makes the collision process more nearly resonant has not been well investigated previously, and thus the present study is expected to shed much light on this effect in general.

DOI: 10.1103/PhysRevA.76.042711

PACS number(s): 34.70.+e, 52.20.Hv, 82.30.Fi

I. INTRODUCTION

In ion-molecule collisions at energies above 100 eV, it has been widely speculated that effects arising from differences in the molecular geometrical structure or isotope, molecular orientation or configuration, and also vibrational state should not have a critical influence on inelastic processes such as ionization and electron capture. This is because the interaction time appears to be more or less independent of their geometrical shapes (isomer or isotope) and there is a huge disparity between the collision time and the rovibrational period of a target molecule. Our recent systematic investigation for electron capture in ion-molecule collisions has revealed a number of phenomena and insights, however. An isomer, an isotope, a steric, and a vibrational (with temperature) effect that have a significant influence on charge transfer were found for hydrocarbons as well as the simpler H₂ and CO molecules in collisions with protons at energies above 100 eV and often even in the few keV regime $\begin{bmatrix} 1-11 \end{bmatrix}$. These insights should significantly alter our previous knowledge for molecular target cases, and should be very important for a variety of applications that utilize such molecular data

For the case of exothermic collisions, even if the initial channel is electronically and vibrationally in the ground state, the target molecular ion produced after the collision is expected to be vibrationally (and rotationally) excited because, in this way, it enforces a near-resonant condition [12]. In our joint experimental and theoretical studies [4-6,11] with such targets as methane, the charge-transfer cross sections with the final target molecular ions existing in a vibrationally excited state have been found to be larger (by several times to an order of magnitude) than those for the production of the vibrational ground state. These features can be easily understood when one extends the concept of resonant or near-resonant conditions to include vibrational as well as rotational quantum states.

Specifically, for the "temperature effect" of the initial vibrational state of the target molecule, in general, a majority of the vibrational excitation energy for a variety of molecules is on the order of ~ 0.1 eV or less. Hence, for collision energies above 100 eV, the relative collision energy is far larger than the energy of the internal motion, and correspondingly, the collision time is much shorter than the vibration period. As a consequence, a projectile is expected to rarely see details of the target structure, that is, the geometrical structure and its vibrational state, before completing the collision. Hence, it has generally been accepted that it should not really matter whether the target molecule is in the ground vibrational state or one of its low vibrationally excited states. Endothermic collisions when the internal energy in the initial channel increases certainly should decrease the energy defect, thereby causing such processes to be more likely to fulfill the near-resonant condition and therefore result in larger cross sections. Indeed, we have found, based on our previous joint experimental and theoretical studies, that electron capture from the lowest vibrationally excited state is larger by a few times to an order of magnitude than that from the corresponding ground vibrational state of target molecules such as CO or CO_2 [3,4,11] below 1 keV. These features can also be understood when one considers the concept of resonant or near-resonant conditions by inclusion of rovibrational states, as pointed out above. This experience clearly indicates that it is a huge obstacle even for energetic particles to overcome a minute barrier such as a rovibrational level in order to reach the final state through transition.

In previous theoretical work we have investigated charge transfer in collisions of H⁺ ions with the ethylene molecule (C_2H_4) [9,10] and discussed the effect of electronic states of the product $C_2H_4^+$ ions as well as the steric effect. However, the vibrational excited states of both parent C_2H_4 molecules and product $C_2H_4^+$ ions were not considered since there were no experimental results available for comparison at that time. In the present study, we carry out a joint investigation for charge transfer in collisions of H⁺ and O⁺ ions with C_2H_4 molecules in which we specifically undertake a more careful examination of the vibration-temperature effect on charge transfer processes.

The following processes are studied:

$$H^+ (or O^+) + C_2 H_4(v) \rightarrow H (or O) + C_2 H_4^+(v') + \Delta E,$$
(1)

where v and v' represent vibrational quantum numbers before and after the collision, respectively, and ΔE is the energy defect. When both the initial and final channels are in the vibration and electronic ground states, the processes studied are exothermic and ΔE is about 3.1 eV [13]. However, if excited vibrational states both in the initial and final channels are taken into account, then this energy defect varies significantly, allowing the process to satisfy a resonant condition to either a greater or lesser degree. As a particular case, if the final vibrational state is in one of these high-lying states, then the energy defect becomes small ($\Delta E \sim 0$).

In the present experiments, we determine such chargetransfer cross sections in the energy range of 0.2 to 3.6 keV by applying an initial growth rate method [14] to the product atomic hydrogen resulting from the charge transfer. For a better understanding of the collision mechanism in a lower velocity regime, charge-transfer cross sections of O⁺ ions colliding with C₂H₄ molecules have been additionally measured in the energy range from 0.28 to 3.6 keV. H and O atoms possess nearly identical ionization potentials of 13.598 eV and 13.618 eV [13], respectively, and hence these two ions are expected to have similar dynamics and cross sections for charge transfer, at least for the energy region above 100 eV. Theoretically we obtain our results by using a molecular orbital expansion method within a fully quantum mechanical as well as a semiclassical formalism. For detailed examination of the collision dynamics, three molecular configurations are specifically considered for close study: a proton approaches parallel to and perpendicularly to the molecular axis with respect to the C=C bond in the C_2H_4 plane, and also from above the plane of the molecule.

II. EXPERIMENTAL METHOD

A detailed description of the present experimental apparatus and methods has been given previously [3–5,11,15–17] and hence, only essential features will be briefly summarized here.

An H⁺ ion beam was extracted from an electron impact ion source and sent into a collision cell filled with the target C_2H_4 gas of high purity (>99.9%). The target gas pressure was measured with a sensitive Pirani gauge [16] which was calibrated with an MKS-Baratron capacitance manometer. After the collisions, both the incident protons and product neutral hydrogen atoms were charge separated with an electrostatic deflector and detected with a microchannel plate position-sensitive detector (MCP-PSD) [17]. The chargetransfer cross sections were derived based upon the growth rate method [14] by fitting the observed fractions of neutral hydrogen atoms to a quadratic function of the target gas thickness.

To ensure that only ground state O⁺ (⁴S) ions were generated, the electron impact energy E_e into the CO₂ molecules was set to below 23 eV. However, this impact energy can still produce small amounts of metastable O⁺ (²D) state ions. We have examined the effect of ions in different electronic states for charge-transfer cross sections of the present target molecules by measuring the variation of neutral atom fractions produced through charge transfer as a function of the electron impact energy in the ion source at a constant target gas density. However, the fractions of the neutral oxygen atoms produced in O⁺+C₂H₄ collisions do not change even if the E_e increases up to 50 eV.

The statistical uncertainties of the cross sections are a few percent for most of the present work. Systematic uncertainties due to the determination of the target thickness, the temperature of target gases and so forth are estimated to be from 10.6% to 14.5% for determining the absolute cross sections. Total experimental uncertainties of the absolute cross sections are given as the quadratic sum of the individual uncertainties involved.

III. THEORETICAL MODEL

The theoretical methods employed are standard and have been described more extensively elsewhere [4–7,9,10]. Hence, only a summary of specific features is described below.

A. Molecular states

Briefly, the adiabatic potential-energy curves and corresponding wave functions are calculated by means of the multireference single- and double-excitation configuration interaction (MRD-CI) method [18–22], with configuration selection and energy extrapolation employing the Table-CI algorithm [20] for efficient handling of Hamiltonian matrix elements for many-electron basis functions (symmetrized linear combinations of Slater determinants). The coupling matrix elements were determined based on the method described in Refs. [23,24].

The atomic orbital (AO) basis set employed consists of contracted Cartesian Gaussian functions. For carbon atoms, a primitive basis (10*s*, 5*p*, 2*d*, 1*f*) contracted to [4*s*, 3*p*, 2*d*, 1*f*] by Huzinaga [25] and Dunning [26] was employed, while the hydrogen basis was (5*s*, 2*p*, 1*d*) contracted to [3*s*, 2*p*, 1*d*] by these authors. The calculations are carried out in the C_{2v} point group, depending on the approach of the proton toward the midpoint of the ethylene molecule along the three principal axes.

The target molecule is frozen by fixing its coordinates while changing those of the proton during collisions. This treatment is reasonable since the present collision time is much shorter, less than 10^{-16} s, than the relaxation time for nuclear motion of 10^{-13} s or longer. Hence, only the internuclear distance *R* between the H⁺ projectile and the midpoint of the C==C bond was varied in the molecular-state calculations. The C==C bond is placed along the *x* axis with its midpoint at the origin of the coordinate system, and C—H bonds all lie in the *xy* plane. The incident projectile approaches the target from three different directions: (a) the proton moves on the *x* axis toward the C atom bisecting the H—C—H bond angle, (b) the proton approaches the midpoint of the C==C bond on the *y* axis, and (c) the proton moves on the *z* axis toward the midpoint of the C==C bond.

B. Vibrationally excited molecules and molecular ions

A correct procedure for including vibrational effects involves the determination of potential energy curves (surfaces) by changing all molecular angles and intranuclear distances and then doing dynamical calculations for nuclear motion such as we have done in our recent study of the H^+/CO system [27]. However, this procedure is too tedious and impractical for polyatomic targets to obtain a simple but intuitively correct physical picture such as is required in the present case. Therefore, as described below, we adopt a much simpler approach. The vibrational levels for ethylene we consider are given in Table I [28]. As can be seen, the lowest vibrationally excited state lies 826 cm⁻¹ above the ground level, and many excited levels are packed closely above this energy. As discussed above, since we are concerned here with collisions above a few hundreds of eV energy, the vibrational motion can be regarded as completely stationary during the collision. Hence, it should be a reasonable procedure to mimic this vibrational effect by changing the electronic energy only. In order to incorporate the effect of the vibrationally excited state in our scattering calculations, we have shifted the potential energies accordingly to match each vibrational level, and reevaluated the corresponding coupling matrix elements based on a perturbative model such as the Landau-Zener-type or Demkov-type methods [29,30] depending upon the scheme of potential curve crossings. The rationale for making such shifts is that the energy of the vibrational states plays a predominant role in the interactions, not the differences in the associated vibrational wave functions themselves. The change in magnitude

TABLE I. Vibrational excitation energy fundamentals for the C_2H_4 molecule [28].

	Fundamental vibrational frequency
Mode	(cm^{-1})
HCC bending	826
Off-plane bending	943
Off-plane bending	949
Twisting	1023
HCC symmetric stretching	1236
HCH asymmetric stretching	1342
HCH bending	1444
CC symmetric stretching	1623
HC symmetric stretching	2989
CH symmetric stretching	3026
CH symmetric stretching	3103
CH asymmetric stretching	3106

of couplings and the position of a curve crossing have decisive influence on dynamics, but these shifts of the potential energies also affect the phase term in coupled equations, which directly reflects on transition probabilities and hence scattering dynamics.

The exact vibrational levels for $C_2H_4^+$ ions produced after charge transfer are not known. However, using the analogy for the H_2 and H_2^+ potential surfaces, the potential curve for the $C_2H_4^+$ ion should possess a somewhat wider parabola in the lower-energy region than that for the C₂H₄ molecule due to diminished bonding strength (from the π orbital in the present case). Therefore, in order for us to reproduce the vibrational levels for $C_2H_4^+$ ions properly, we varied (lowered) those values in Table I for the C_2H_4 molecule by an amount of 10-15%, and adopted these values for the vibrational levels of the molecular ion. These values may not be sufficiently accurate for many purposes at the level of spectroscopy, but the important point here is to show how the near-resonant condition in the final state from rovibrational states will also alter the dynamics relative to that of the ground state, so this approximation should be sufficiently accurate for the present purposes.

C. Collision dynamics

Fully quantum-mechanical and semiclassical approaches within a molecular representation were employed, that is, the so-called molecular-orbital close-coupling (MOCC) method, in which dynamical transitions are driven by nonadiabatic couplings [29,30]. The quantum-mechanical MOCC method has been employed below a few 100 eV, while a semiclassical MOCC method was used for higher energy, but results from both approaches are found to be in good accord (within 10%) at 100 eV. Hence, the results shown below are from the semiclassical MOCC procedure.

The total wave function for scattering in a quantummechanical approach is a product of the electronic and nuclear wave functions, while it is described as a product of a time-dependent coefficient and an electronic wave function in the semiclassical picture.

Substitution of the total scattering wave function in a quantum-mechanical formalism into the time-independent Schrödinger equation yields coupled, second-order differential equations for the nuclear motion. It is computationally convenient to solve the coupled equations in a diabatic representation (see detailed procedures in Ref. [29]). The coupled equations are solved numerically to obtain the scattering matrix element, and the differential cross section (DCS) as a function of scattering angle is then obtained by the standard procedure. Integration of the DCS over all angles gives the cross sections. For the semiclassical representation, substituting the total wave function into the timedependent Schrödinger equation yields a set of first-order coupled differential equations for time-dependent coefficients. By solving them, one can obtain a transition amplitude and integration of the product of the square of the amplitude over impact parameter yields the cross sections.

In the present calculations, we employed up to seven-state close-coupling treatments with molecular states arising from the initial $[H^++C_2H_4]$, charge transfer $[H+C_2H_4^+]$, target excitation $[H^++C_2H_4^+]$, and charge transfer with excitation $[H+C_2H_4^{+*}]$ channels.

IV. RESULTS AND DISCUSSION

A. Adiabatic potentials

Since details of the characteristics of the potentials and couplings have already been discussed earlier in Refs. [9,10], only a summary of these results is given below. Figures 1(a)-1(c) contain adiabatic potentials for the present collision system for three different configurations (a), (b), and (c), respectively. The equilibrium geometry of the target molecule is fixed in the calculations, that is, only the position of the approaching proton is varied. The initial $[H^++C_2H_4]$ state is found at the third from the bottom (B state), while the ground $[H+C_2H_4^+]$ state after charge transfer lies lowest (X), and the second (A) and the fourth (C) correspond to electronically excited $[H+C_2H_4^{**}]$ states. The nature of these excited ionic states has been discussed in Ref. [9] (cf. Table 2 of Ref. [9]). The active (open-shell) electron in the first two $C_2H_4^+$ states (X and A) possesses π and in-plane p_{ν}^- character, respectively, while in the second excited state (C) it is σ . The nature of these states changes in an individual manner depending on the direction of approach of the proton, as is evident from comparison of Figs. 1(a)-1(c). As a specific characteristic of the potential curves for the (a) and (b) configurations, the initial state, the third from the lowest, crosses the first and second states because of the different symmetry, while the initial and fourth states show rather parallel nature at all R. Therefore, for (a) and (b), transition through angular coupling is expected to be more efficient than that by radial coupling on the low-energy side. For the (c) configuration, except for the ground-state potential, all curves are repulsive and hence increasing with decreasing R, and they do not show any hint of strong avoided crossings among them be-



FIG. 1. Computed potential energy curves for the lowest channels of the $(H+C_2H_4)^+$ system for three approaches of the proton (from Ref. [10]).

cause the interactions are due to relatively weak polarization potentials, suggesting a Demkov-type mechanism [30] for charge transfer. For the vibrationally excited state in the initial channel, that is, the *B* state, we have shifted its potential to match a given vibrational energy as shown in Table I. Since the vibrational excitation energies we consider here are less than 1 eV, such potential shifts are not distinguishable graphically. For the contribution from the final vibrational state after charge transfer, we similarly shift the potentials for the *X*, *A*, and *C* states to enforce the resonant condition through the coupled equations.

TABLE II. Charge-transfer cross sections of H^+ ions colliding with C_2H_4 molecules.

H ⁺ energy (keV)	Cross sections $(10^{-16} \text{ cm}^2/\text{molecule})$
0.200	32.8±4.5
0.360	27.6±3.3
0.660	25.0 ± 3.0
1.20	24.5 ± 2.6
2.00	23.4±2.5
3.60	21.6±2.3

B. Experimental results for H⁺ and O⁺ impact

The present experimental cross sections for charge transfer by H⁺ ions and O⁺ ions from C₂H₄ molecules are given in Tables II and III, respectively. The present theoretical and experimental data are both shown as a function of the incident energy per nucleon in Fig. 2, together with the recommended values by Janev, Wang, and Kato [31]. These authors compiled our previous cross-section data [5] for CH₄, C₂H₂, C₂H₆, and C₃H₈ along with other experimental results for the charge-transfer process in H⁺+C_xH_y collision systems (where x=1-4 and $1 \le y \le 2x+2$). The data were then fitted to an analytical formula describing this group of chargetransfer cross sections. On this basis, these authors were able to predict cross-section values for collision systems such as H⁺+C₂H₄ and C₃H₄, for which no experimental data were as yet available.

To the best of our knowledge, cross sections for the C_2H_4 molecule have not been reported previously at energies below 30 keV/u. The present charge-transfer cross sections of H⁺ ions gradually decrease as the collision energy increases. While the present charge-transfer cross sections for O⁺ ions are almost energy independent, they are found to be similar to those of H⁺ ions for 0.2 keV/u collision energy for which data exist for both systems. The predicted values by Janev, Wang, and Kato [31] are in good accord with the present data at above 0.1 keV/u, but are slightly larger than the present measurements for O⁺ ions below 0.1 keV/u. Also note that their predicted cross-section values appear to show an increasing trend with decreasing energy.

The previous cross sections calculated by Suzuki *et al.* [10] that have considered only the vibrational ground states

TABLE III. Charge-transfer cross sections of O^+ ions colliding with C_2H_4 molecules.

O ⁺ energy		Cross sections
(keV)	(keV/u)	$(10^{-16} \text{ cm}^2/\text{molecule})$
0.280	0.0175	30.7 ± 4.6
0.360	0.0225	28.9 ± 3.7
0.660	0.0413	26.7 ± 3.5
1.20	0.0750	29.7 ± 3.5
2.00	0.125	29.4 ± 3.5
3.60	0.225	29.8±3.5



FIG. 2. Charge-transfer cross sections for collisions of H^+ and O^+ ions with C_2H_4 . Solid and open circles are the present experimental results for H^+ and O^+ ions, respectively. Solid curve is for the results for case (iii), i.e., both initial and final states are in vibrationally excited states. Dashed curve is for case (i), that is, the vibrational ground initial state and vibrationally excited final state. Dotted curve gives the previous theoretical results by Suzuki *et al.* [10]. Dotted-dashed curve gives the predicted values by Janev, Wang, and Kato [31].

of both the parent molecule and the product molecular ion are found to have a constantly decreasing trend, even though their results are of the same order of magnitude as in the present measurements. As the energy decreases, the predicted cross section decreases to a value of 1.5×10^{-15} cm² at 0.2 keV. This decreasing feature, which is not verified in the present measured results, is typical for the case of a nonresonant collision, and may be due to the absence of vibrational effects in their calculations [10]. Note that all theoretical results beyond 5–6 keV may not be sufficiently accurate since this is the energy region where the present molecular picture may begin to break down. Therefore, these results are only considered as a reference.

C. Vibrational effect

We carry out the calculations by including 12 vibrationally excited states in the initial channel, all of which have excitation energies less than 0.2 eV, as shown in Table I. Furthermore, the effect of the vibrational states in the final ionic channel is also examined in order to judge to which degree this effect in the final channel governs the resonant condition. It would be quite natural to expect based upon some experimental evidence in low-energy reactive collisions that after charge transfer, the residual molecular ion thus formed should be in one of those highly excited vibrational and rotational states. Therefore, these vibrational states in the final channel should also be taken into account explicitly. Vibrational states considered for the final channel (that is, for the $C_2H_4^+$ molecular ion) are taken up to v'=5. As can be seen in Figs. 1(a)-1(c), if the initial B channel is in its vibrational ground state, then the B and A states are energetically close and are coupled strongly. There are two possible consequences for the contribution from the vibrational effect: (1) it is apparent that if the *B* vibrational state is excited, then it becomes energetically closer to the C state, and begins to have stronger mixing with the latter through radial coupling. As a result, the transition probability between these two states is likely to increase, i.e., there is enforcement of the near-resonant condition; (2) if the *B* state is in its vibrational ground state, but the final *A* vibrational state is excited, then the resonant condition is again strengthened, making the transition more favorable. Therefore, it is essential to examine two types of vibrational effects, i.e., for the initial as well as the final state.

Experimentally, these vibrationally excited molecular states are expected to constitute a total population of more than 15% at room temperature (the ratio of the ground vibrational state to a sum of all vibrationally excited states). The present calculations thus obtained by including the population distribution of the vibrational state are also added in Fig. 2. These new calculated results are closer to the present measurements than the previous calculations of Suzuki et al. [10]. As described above, we have examined three different cases for reducing the energy defect: (i) charge transfer from the initial (B) vibrational ground state to the vibrationally excited molecular ion (X and A states), (ii) charge transfer from the initial vibrationally excited state to the vibrational ground state of the molecular ion (A and C states), and (iii) charge transfer from the initial vibrationally excited state to the X, A, and C vibrationally excited states. The calculated results for cases (i) and (iii) are included in Fig. 2. A brief summary for charge-transfer cross sections when vibrational excitation in both channels is included is in order here. By increasing the energy of vibrational levels in the initial and final channels, the energy defects between the *B* and *C* states and the B and A states decrease, respectively, compared to the case for vibrational ground states in both channels. Correspondingly, the locations of curve crossings move toward the inner region. These changes are much more favorable for charge transfer to fulfill the near-resonant condition. On the average, dominant charge-transfer cross sections for C and A states are found to increase by 30-40% for all configurations at 1 keV, compared to those of earlier results by Suzuki et al. [10]. This observation is a clear manifestation of the vibrational effect.

Both sets of theoretical results are found to be in improved agreement compared to the previous results of Suzuki et al. [10]. As is apparent, the results for case (iii) are found to agree very closely with the measurements in the entire energy region studied, although the present experimental values are still somewhat smaller in magnitude, but the agreement is much better than for case (i). The results obtained for case (i) are rather energy independent, but still represent an improvement over the earlier results with regard to the decreasing feature in the earlier work. The magnitude of cross sections for all three cases is similar. However, only case (iii) gives reasonable accord with the energy dependence found in the measurements, that is, a slowly increasing trend with decreasing energy. This increasing feature is a manifestation of near-resonant charge transfer enforced through the contribution from vibrational states in the initial as well as final channels. Since the energy defect narrows as the vibrational excitation increases in the initial as well as final channels and hence the magnitude of corresponding couplings increases, the near-resonant condition is fulfilled as a consequence, making the transition more favorable. If the vibrational state in the final channel is neglected, the results show a much weaker energy dependence that lies intermediate between the present and previous theoretical results. When the final vibrational states are taken into account in the calculation, the energy dependence begins to have better agreement with the measurements. Even though our present calculations are in good accord with the present measurements with regard to their energy dependence, the magnitude of the present theoretical results barely touches the edge of the lower limit of the measurements, and a sizable difference still remains. Probably, the combination of the precision of the MOs employed and the indirect treatment of vibrational states both in the initial and final channels in the collision calculation may be responsible for the remaining differences. More rigorous, explicit inclusion of vibrational levels would be desirable to resolve this discrepancy. Nevertheless, it is clear that even a minute amount of barrier of less than 1 eV presents a difficult obstacle for energetic particles with keV kinetic energy to overcome. Therefore, based on the present study, it seems highly probable that even rotational excitation of the target molecule may be expected to significantly influence the ionization and charge-transfer processes at low energies.

Apparently, the "temperature effect" in the initial state becomes more significant as the collision energy decreases, and the difference between the present and earlier results should widen. From this analysis as well as the reasonable agreement obtained, it is clear that vibrationally excited molecules are already present in the sample of ethylene used for the experiments and apparently they play a significant role for dynamics. Hence, the present investigation indicates that it is very important to consider rotation and vibration effects for ionization and charge transfer even in the neighborhood of keV-energy collisions, and the analysis of the experimental data must be carried out carefully based on these considerations. The effects of rovibrational states have been completely ignored earlier in calculations of keV collisions, but the present investigation clearly suggests that such a treatment is not completely justified.

It should be mentioned that collisional vibrational excitation is considered to be important below 100 eV or so, and hence, in the present energy domain, this process would be secondary. Also, after charge transfer, various kinds of molecular ions are formed, and these species are, in many cases, short-lived and hence undergo fragmentation. A discussion of fragmentation processes and fragmented species thus produced from the present molecule has been given earlier [10].

V. SUMMARY

We have measured charge-transfer cross sections for collisions of H^+ and O^+ ions with C_2H_4 molecules from 0.018 keV/u to 4 keV/u, and the cross sections for O^+ impact fit in well with those for H^+ impact in the energy regions in which the data overlap. The present theoretical treatment, which takes the vibrational effects of the initial and the final states into account, agrees well with the measurements in the entire energy region. From the present investigation, it has become clear that even a very small barrier arising from rotational and vibrational states is very difficult for energetic particles to overcome. The transition is likely to occur more easily when a small amount of vibrational energy is added, thereby resulting in a larger cross section. Therefore, there is an indication that even rotational excitation may significantly influence the dynamics for ionization and charge-transfer processes in slow collisions. This expected effect should be more carefully examined in future work, since almost all of the molecules involved in collision processes are in a highly excited rotational state.

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ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science, Sport, Culture and Technology, the Japan-Germany Collaborative Research Program of the Japan Society for Promotion of Science, Cooperative Research Grant from National Institute for Fusion Science, Japan [to two of the authors (T.K., M.K.)], and also by Grant No. BU 450/7-3 of the Deutsche Forschungsgemeinschaft [to one of the authors (R.J.B.)].

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