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LONG RANGE CONTRIBUTIONS TO VIBRATIONAL EXCITATION IN MODERATE ENERGY ION-MOLECULE PROCESSES

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An estimation of the long range contributions is made to vibrational energy transfer in ion-diatomic molecule collisions in the energy region of a few hundred eV. The calculations are based on the linearly forced harmonic oscillator theory and assume that vibrational excitation takes place through the linear dependence of the polarizability of the diatom on the vibrational coordinate. When the diatomic molecule possesses a permanent dipole moment a similar linear dependence is assumed for the dipole moment. The results of the method are compared to the experimental findings for $Li^+ + N_2$ and $Li^+ + CO$ collisions at the energy region of a few hundred eV.

1. Introduction

Several studies have been made recently on vibrational excitation induced in ion-molecule collisions, for ion energies ranging from a few eV up to a few hundred eV. Most of these studies have been concentrated in the low energy region and the differential cross sections have been mainly examined. Analysis of the classical scattering in this region has provided interesting informations about how certain properties of the interaction potential influence the transition probabilities and their angular distribution.

Similar studies have been carried out at the intermediate energy range 10^2—10^3 eV where the process is characterized by the small energy defect compared to the ion velocity. Such investigations provide additional information about the

absolute total cross sections of these processes, which are not easily determined from differential cross section measurements. At the energy range of a few hundred eV integral cross sections may be easily determined since the scattered ions are concentrated in a very narrow angle. Herrero and Doering[1] measured the forward component of the total cross section for vibrational excitation of H_2 by proton impact from 100 to 1500 eV and they obtained very large values of the order of 10^{-16} cm^2 for the excitation of the first vibrational level. Also broad maxima were observed in the variation of the cross section with increasing ion velocity. For energies above 100 eV they found that the peak intensity of the ion energy loss spectra is a rapidly decreasing function of the deflection angle. Kabayashi et al. studied the vibrational excitation of CO, CO_2, N_2O[2] and NO[3] by Li^+ impact from 70 to 1500 eV and they found that excitation takes place in strongly forward scattering above 400 eV. The angular distribution of the inelastically scattered Li^+ ions associated with the excitation of the $v = 1$ level of CO was found to decrease rapidly to zero at an angle of 0.4 degrees for an ion energy of 414 eV. Finally differential cross sections were obtained by Lebéhot and Cambargue[4] for the vibrational excitation of H_2, induced in collisions with He^+ at 510 eV. The differential cross section was found to be a rapidly decreasing function of the laboratory scattering angle, in the range 0.0 to 1.0 degrees.

The scattering pattern is naturally quite different for such differences in the incident ion energy. Usually in the range below 100 eV the integral cross section increases monotonically with increasing ion velocity. As the ion energy is further increased a broad maximum is observed and then a slow decrease with increasing energy. Such behaviour indicates an exponential type dependence of the excitation probability on the collision energy, which may be calculated from the linearly forced harmonic oscillator model[5-7]. This model describes quantitatively correctly the exchange of energy between the translational and vibrational degrees of freedom in collisions of an atom with a harmonic oscillator and its great value lies on the fact that its solution is exact. Thus it has found wide applicability in numerous collision processes where the final distribution of vibrational states on a single potential energy surface is studied and as such it has been also used to explain vibrational excitation in ion-molecule collisions with good success. Among the recent applications is the DECENT model suggested by Giese and Gentry to explain vibrational excitation in collisions of H^+ with H_2, HD and D_2[8]. Also Krüger and Shinke[9] have used it fot $H^+ + H_2$ systems, Ellenbroek and Toennis[10] for ion-spherical top molecules and Iwamatsu et al. for ion-polar molecule systems[11].

In the present study a simple, phenomenological theory is developed within the framework of the impact parameter approximation[12] based on the linearly forced harmonic oscillator model. The model explains fairly well the total cross sections for vibrational excitation, observed in collisions of ions with simple molecules at moderate energies. Because at these energies vibrational excitation occurs mainly in strongly forward scattering where the large impact parameter collisions consist the most important contribution to the total cross section, we assume that the long range, electrostatic type interaction between the ion and the molecule is the main mechanism by which vibrational excitation is invoked. This assumption is not unreasonable since generally, small angle vibrational inelastic scattering of molecules by ions is attributed to long range electrostatic forces[12] whereas wide angle scattering is produced primarily by the short range interactions. The method

is applied to the inelastic scattering of N_2 and CO by Li^+ impact and the results are compared with the available experimental data.

2. *Theory*

We consider the collision of a structureless ion with a diatomic molecule in the process

$$A^+ + BC(v = 0) \rightarrow A^+ + BC(v = 1, 2, \ldots). \quad (1)$$

Fig. 1 shows a diagramatic representation of the coordinate system of such a collision.

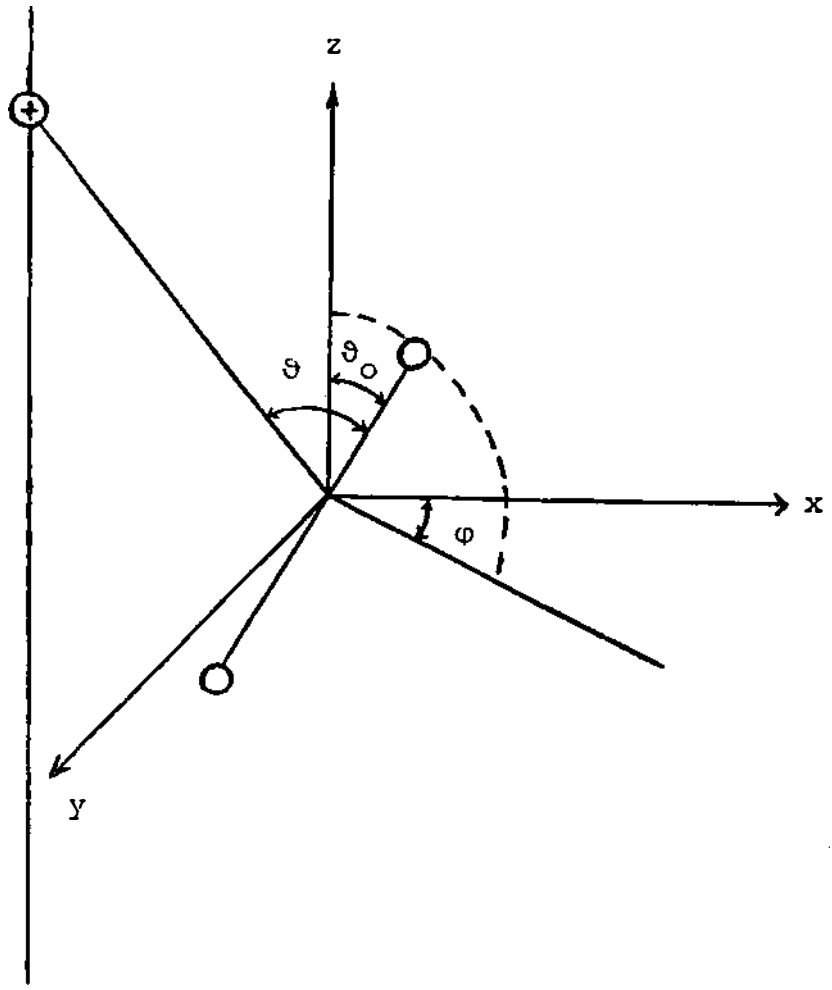

Fig. 1. Diagram showing the coordinate system of the ion-diatom collisions.

The model is based on the following assumptions and approximations:

(1) The rotational motion of the molecule is neglected during the collision, i.e., the sudden approximation is adopted.

(2) The impact parameter approximation is used in which the trajectory is taken to be linear with constant velocity and impact parameter b.

(3) The interaction potential of an ion and a molecule is modelled by the polarization potential expressed in terms of the isotropic part of the polarizability of the molecule and used with an appropriate cut-off parameter. When the diatomic molecule possesses a permanent dipole moment the charge-dipole potential is added.

(4) Molecular vibration is assumed to be harmonic. We accept that excitation takes place through the linear dependence of the polarizability on the vibrational coordinate. Similar dependence is added for the permanent dipole moment in the case of polar molecules.

According the assumptions mentioned above the interaction potential between an ion and a nonpolar molecule is approximated by the long range ion-induced dipole potential $V(r) = -q^2\alpha/2r^4$ where q is the charge on the ion, α is the polarizability of the molecule and r is the distance between the ion and the center of mass of the molecule. Letting the polarizability be expanded as

$$\alpha(x) = \alpha_0 + \alpha' x + \ldots \tag{2}$$

where x represents the displacement of the oscillator from the equilibrium position, the polarization interaction becomes

$$V(r, x) = -q^2\ \alpha(x)/2r^4. \tag{3}$$

In general the Hamiltonian of the colliding partners the diatomic molecule BC and the ion A^+ may be written in the form[7]

$$H_{A^+-BC} = H_{BC} + T_{A^+-BC} + V(r, x) \tag{4}$$

where H_{BC} is the Hamiltonian of the isolated molecule BC; T_{A^+-BC} is the relative kinetic energy of the system; and $V(r, x)$ is the potential responsible for the interaction between A^+ and BC. On the assumption that x is small, $V(r, x)$ may be approximated to sufficient accuracy by the first two terms in the expansion

$$V(r, x) = W(r) - x\,F(r) \tag{5}$$

where

$$W(r) = V(0, r) = -q^2\,\alpha_0/2r^4 \tag{6}$$

and

$$F(r) = -\left[\frac{\partial V(r, x)}{\partial x}\right]_{x=0} = q^2\,\alpha'/2r^4. \tag{7}$$

With this approximation Eq. (4) is transformed into

$$H_{A^+-BC} = H_{BC} + T_{A^+-BC} + W(r) - xF(r). \tag{8}$$

This is exactly the problem of an ideal harmonic oscillator subject to an external time-dependent force. The time dependence of the force may be established through the time dependence of the trajectory $r(t)$. In the impact parameter approximation the straight line trajectory $r(t)$ is obtained by

$$r(t) = (b^2 + v^2 t^2)^{1/2}. \tag{9}$$

The transition probability for going from state $v = 0$ to a state $v = n$ is given by[7]

$$P_{0n} = (\varepsilon^n/n!) \exp(-\varepsilon) \tag{10}$$

where ε is the average number of vibrational quanta transferred to the oscillator. ε is given by

$$\varepsilon = (1/2\,\hbar\omega m) \left| \int_{-\infty}^{\infty} F(t) \exp(i\omega t)\, dt \right|^2 \tag{11}$$

where ω and m are the angular frequency and reduced mass of the oscillator, respectively. It corresponds exactly to the classical result for the energy transmitted to the system during all time[13]

$$\Delta E = (1/2\,m) \left| \int_{-\infty}^{\infty} F(t) \exp(i\omega t)\, dt \right|^2. \tag{12}$$

Having calculated the transition probability P_{0n} from Eq. (10), the total cross section may be obtained from

$$\sigma_{0n}(v) = 2\pi \int_{b_0}^{\infty} P_{0n}(b, v)\, b\, db \tag{13}$$

where b_0 is appropriately chosen cut-off parameter.

When the diatomic molecule BC possesses a permanent dipole moment the ion-dipole interaction may be treated in a similar manner. The permanent dipole moment is expanded as

$$\mu(x) = \mu_0 + \mu' x + \ldots \tag{14}$$

The total interaction $V(r, x)$ takes the form

$$V(r, x) = -q^2\, \alpha(x)/2r^4 - q\mu(x) \cos\vartheta(t)/r^2, \tag{15}$$

and the time dependent external force becomes

$$F(t) = q^2\, \alpha'/2r^4(t) - q\mu' \cos\vartheta(t)/r^2(t). \tag{16}$$

Here the potential involves the anisotropic factor of $\cos\vartheta(t)$, where $\vartheta(t)$ is the angle between the dipole axis and the distance of the ion from the center of mass of the molecule. It depends both on the time and the initial orientation (ϑ_0, φ) of the dipole axis with respect to the velocity of the incident ion. Analyzing $\vartheta(t)$ Eq. (16) becomes

$$F(t) = q^2\,\alpha'/2r^4(t) + q\,\mu'\,vt\cos\vartheta_0/r^3(t) + q\,\mu'\,b\sin\vartheta_0\cos\varphi/r^3(t). \qquad (17)$$

By substituting into Eq. (11) ε is determined and then the transition probability and the total cross section may be calculated in principle from Eqs. (10) and (13), respectively.

A weak point of the theory that must be carefully examined is the choice of the cut-off parameter b_0. From the physical consideration of the problem b_0 must correspond roughly to the region where the long range attractive potential becomes invalid and the potential energy function is entirely dominated by the strong, short range, repulsive forces. It is therefore a reasonable assumption to take b_0 to be the hard-sphere collision diameter. An analogous assumption was made by Sharma and Brau[22] in their approximate calculation of vibrational energy transfer in N_2-CO_2 mixtures, where they expressed the transition probability in terms of the hard-sphere collision diameter. For the $Li^+ - N_2$ and $Li^+ - CO$ systems the short range part of the potential is well known and thus estimation of this parameter is fairly trivial.

3. *Applications*

(1) *Ion-nonpolar molecule systems*

Eq. (7) allows one to treat Eq. (11) analytically and the result is

$$\varepsilon = \frac{\pi^2\,q^4\,\alpha'^2}{32\,\hbar\,\omega\,m}\frac{}{v^2\,b^6}\left(1+\frac{\omega b}{v}\right)^2 e^{-2\omega b/v}. \qquad (18)$$

The total cross section for the $v=0$ to $v=1$ transition is found to be

$$\sigma_{01} = \left(\frac{3\pi^3\,q^4\,\alpha'^2\,\omega}{96\,\hbar\,\omega\,mv^3\,b_0^3} + \frac{\pi^3\,q^4\,\alpha'^2}{64\,\hbar\,\omega\,mv^2\,b_0^4}\right) e^{-2\omega b_0/v}. \qquad (19)$$

Specific application to $Li^+ - N_2$ systems requires the value of the polarizability derivative which is taken 1.33×10^{-16} cm^2 according the values cited in the literature[14,15]. Very important is the choice of the cut-off parameter b_0. From the ab initio calculations of Staemmler[16,17] and the experimental studies of Kita et al.[18] b_0 is estimated to be around 0.22 nm. In Fig. 2 σ_{01} is plotted vs. the ion energy for this value of the cut-off parameter. In the experimental studies of Kobayashi et al. the cross section for the $0\rightarrow1$ excitation was measured and found of the order of 10^{-18} cm^2. Therefore the choice made is not unreasonable and the calculated integral cross section as shown in Fig. 2 is of the same order.

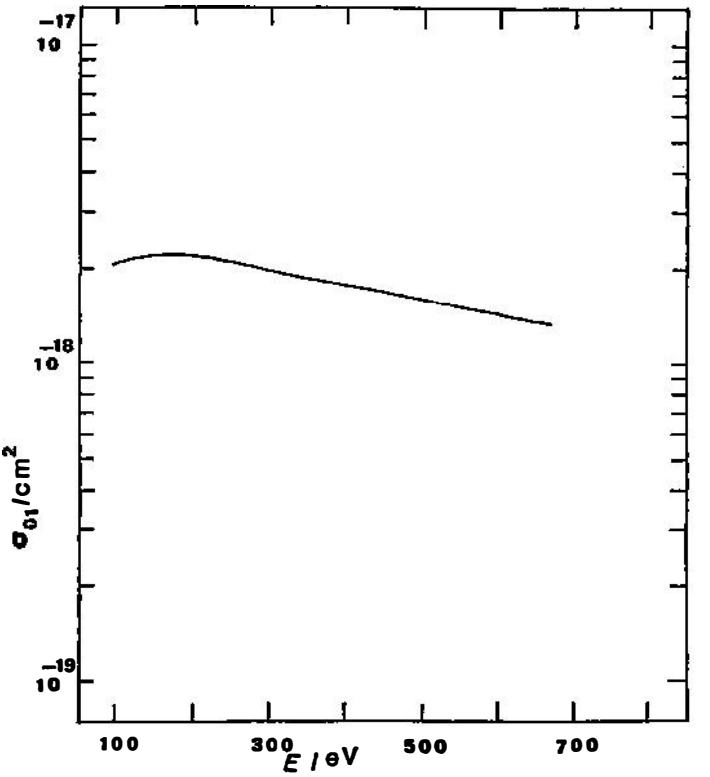

Fig. 2. Total cross section for $0 \to 1$ excitation of N_2 by Li^+ as a function of the ion energy.

(2) *Ion-polar molecule systems*

For the ion-polar interaction ε is found to be

$$\varepsilon = \frac{\pi^2 q^4 a'^2}{32 \hbar \omega v^2 b^6} \left(1 + \frac{\omega b}{v}\right) e^{-2\omega b/v}$$

$$+ \frac{2\mu'^2 q^2 \omega^2}{\hbar \omega m v^4} \ll \sin^2 \vartheta_0 \cos^2 \varphi \, K_1^2(\omega b/v) + \cos^2 \vartheta_0 \, K_0^2(\omega b/v) \gg \qquad (20)$$

since the cross terms on taking the orientation average vanish. The brackets indicate appropriate average over the orientation angles ϑ, φ and $K_1(x)$, $K_0(x)$ are modified Bessel functions. With this result for ε Eq. (13) cannot be evaluated exactly in analytical form. Estimation though of the cross section σ_{01} may be made by considering the asymptotic expansion of modified Bessel function[19,20] up to desired accuracy:

$$K_\nu(x) \sim (\pi/2x)^{\frac{1}{2}} e^{-x} \left\{1 + \frac{\mu - 1}{8x} + \frac{(\mu - 1)(\mu - 9)}{2!(8x)^2} + \ldots\right\} \qquad (21)$$

where $\mu = 4v^2$. The dipole moment derivative μ' was taken from approximate dipole moment functions for the $X^1\,\Sigma^+$ state of CO, calculated for several configuration wave functions and fitted to a four term power series expansion[21]. Thus the value of 1.04×10^{-19} C was used. The results are shown in Fig. 3 where σ_{01} is plotted against the incident ion energy, for the same value 0.22 nm of the cut-off parameter and they are compared to the experimental data. We see that the agreement is fairly good and the magnitude of the cross section is predicted with a fair degree of accuracy.

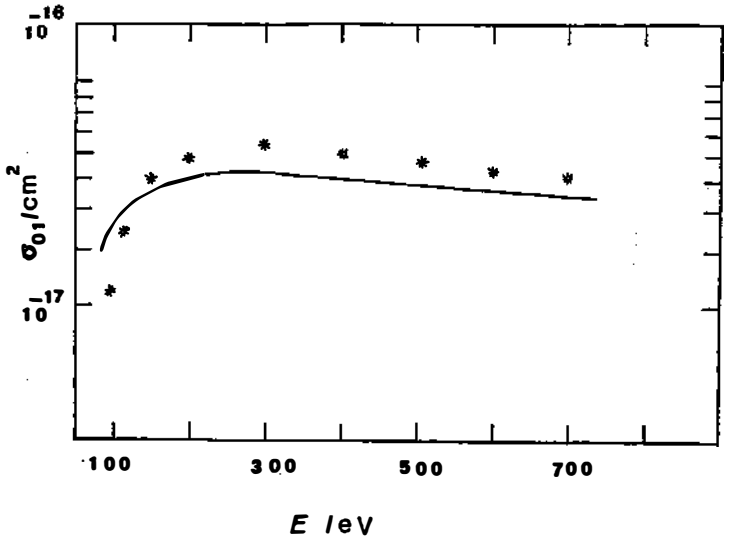

Fig. 3. Total cross section for $0 \rightarrow 1$ excitation of CO by Li^+ impact as a function of the ion energy. The crosses represent experimental points and they are read from graph (see Ref. 2).

Preliminary comparison of the results with a more rigorous approach[23] using a long range potential energy function by fitting the ab initio surfaces, shows that despite its simple form the model provides a useful estimate of the vibrational energy transfer process.

4. Discussion and comparison with other theories

The present approach attempts to estimate integral cross sections for the ion-molecule vibrational excitation process based on the assumption that the vibrationally inelastic scattering arises mainly from grazing collisions. This assumption means that the forward component of the vibrational total cross section consists the major part of it, leading to the conclusion that wide angle scattering at this energy arising from small impact parameter collisions leads to other channels such as elastic scattering or charge transfer processes. Indeed, this is what is found experimentally. As mentioned before the angular distribution of the scattered ions with energy loss associated with the vibrational excitation process was found to be confined in a very narrow region around the distribution of the primary beam

Also the transition probability for similar processes e. g. the $He^+ - H_2$ system was examined as a function of the impact parameter[4]. What was found is that this probability rises from zero for a certain value of the impact parameter and increases with increasing b until it reaches a maximum. Then it starts to decline with further increase in b. This decline in the very large impact parameter region is natural since very distant collisions must have no effect, keeping the cross section from becoming infinite. What is interesting though is that the transition probability increases with increasing b in the range of impact parameters of practical interest for the process under consideration.

It is instructive to examine from the physical point of view how this behaviour results. At the region of very large impact parameters the relationship between the vibrational motion $x(t)$ and the force function $F(t)$ may be easily seen. As the force builds up, the diatomic molecule begins to strech reaching a maximum extention at some time A after the force has peaked. Then since the maximum excursion in x occurs before the driving force decays to zero at some later time B, between times A and B the force opposes the vibrational motion, leaving the molecule somewhat less excited than it would have been if the force has terminated abruptly at time A. At impact parameters around the maximum of the transition probability the driving force acts essentially over the same period of time as before but has a magnitude considerably larger than in the previous case as indicated by Eqs. (7) and (9). The value of x reaches a larger maximum value and thus the maximum excurtion occurs later in time after the acting force has decayed to zero. The distortion suffered by the oscillator at a time A remains uneffected and results in greater vibrational excitation. Finally we come to collisions at small impact parameters which result in very little vibrational excitation despite the strong driving force. Initially the stretching force and the consequent positive acceleration in x are greater than in the large impact parameters cases. In this case though the ion is determined to pass eventually close enough to the nearest nucleus of the molecule and will encounter the repulsive wall of the potential. The driving force becomes negative for a brief time and exercises a strong compressing effect on the oscillator. These effects combine to stop the motion of x abruptly. The second positive branch of the forcing function acts to remove almost exactly the vibrational energy deposited in the molecule by the first branch. As a result we have the production of small excitation energy in the collision products because of partial cancellation of strong, counterparting forces.

We would like to compare the results of the present method to the predictions of other theories which try to explain the behaviour of these particular systems. Kobayashi et al.[2] have used the first Born approximation to explain their experimental findings. Our results are pretty close to their predictions.

The present method is also close to the model presented by Iwamatsu et al.[11]. In their work they calculate the transition probability from the Poisson distribution

$$P_{0n} = (|a|^{2n}/n!) \exp(-|a|^2), \tag{22}$$

where a is obtained from

$$a = (1/ih) \int_{-\infty}^{\infty} V(R(t)) \exp(i\omega t)\, dt \tag{23}$$

and the quantity $V(R(t))$ is defined in the equation

$$\langle n|V(Q, R(t))|\, n-1\rangle = n^{\frac{1}{2}}\, V(R(t)). \tag{23}$$

$V(Q, R(t))$ is the ion-dipole interaction potential and Q the vibrational coordinate. This method is directly associated to the spetroscopic transition matrix elements of the permanent dipole moment by which vibrational transitions take place. In contrast to this procedure we have applied the linearly forced harmonic oscillator theory to ion-molecule collisions for both polar and nonpolar molecules and our results are in good agreement with theirs in the case of polar molecules.

In summary we may say that the theory presented seems to provide a useful phenomenological estimation of the long range contributions to vibrational excitation induced in ion-molecule collisions.

References

1) F. A. Herrero and J. P. Doering, Phys. Rev. **A 5** (1972) 702;
2) N. Kobayashi, Y. Itoh and Y. Kaneko, J. Phus. Soc. Jpn. **45** (1978) 615;
3) N. Kobayashi, Y. Itoh and Y. Kaneko, J. Phys. Soc. Jpn. **46** (1979) 1399;
4) Lebéhot and R. Cambargue, J. Phys. B **15** (1982) 1771;
5) P. Pechukas and J. C. Light, J. Chem. Phys. **44** (1966) 3897;
6) M. J. Child in *Theoretical Chemistry*, ed. W. H. Miller (Plenum, New York, 1976);
7) E. E. Nikitin, *Theory of Elementary Atomic and Molecular Processes in Gases* (Clarendon, Oxford, 1974), p. 41;
8) C. F. Giese and W. R. Gentry, Phys. Rev. **A 10** (1974) 2156;
9) H. Krüger and R. Shinke, J. Chem. Phys. **66** (1977) 5087;
10) T. Ellenbroek and J. P. Toennis, Chem. Phys. **71** (1982) 309;
11) M. Iwamatsu, Y. Onodera, Y. Itoh, N. Kobayashi and Y. Kaneko, Chem. Phys. Lett. **77** (1981) 585;
12) D. Richards, J. Phys. B **15** (1982) 1499;
13) L. D. Landau and E. M. Lifshitz, *Mechanics* (Pergamon, Oxford, 1976);
14) M. Lipeless, J. Chem. Phys. **51** (1969) 1252;
15) M. A. Morrison and P. J. Hay, J. Chem. Phys. **70** (1979) 4034;
16) V. Staemmler, Chem. Phys. **7** (1975) 17;
17) V. Staemmler, Chem. Phys. **17** (1976) 187;
18) S. Kita, K. Noda and H. Inoye, Chem. Phys. **7** (1975) 156;
19) M. Abramovitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1970), p. 378;
20) I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, New York, 1965), p. 963;
21) K. Kirby-Docken and B. Liu, J. Chem. Phys. **66** (1977) 4309;
22) R. D. Sharma and C. A. Brau, Phys. Rev. Lett. **19** (1967) 1273;
23) A. M. Kosmas, in preparation.

DOPRINOS DUGO-DOSEŽNIH SILA VIBRACIJSKIM POBUĐENJIMA U SUDARIMA ION-MOLEKULA KOD SREDNJIH ENERGIJA

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Načinjena je ocjena doprinosa dugo-dosežnih sila na vibracijske prijelaze u sudarima ion—dvoatomska molekula u energijskom rasponu od nekoliko stotina eV. Rezultati su uspoređeni s eksperimentalnim mjerenjima za $Li^+ + N_2$ i $Li^+ + CO$ sudare, u istom energijskom intervalu.