CROATICA CHEMICA ACTA CCACAA 58 (2) 169—177 (1985)

CCA-1569

YU ISSN 0011-1643
UDC 541
Original Scientific Paper

On Some Aspects of Rotationally Inelastic Polarized Molecule-Flat Surface Scattering

Z. Bačić

Institute of Physics of the University, P.O.B. 304, 41001 Zagreb, Croatia, Yugoslavia

and

S. D. Bosanac

Rugjer Bošković Institute, P.O.B. 1016, 41001, Zagreb, Croatia, Yugoslavia

Received October 4, 1984

Polarized molecule-flat surface collisions are investigated for the case when the molecule is initially prepared in a certain rotational slate and when its rotational angular momentum j is aligned parallel to the surface. It is shown that the occurence of two rainbow peaks in Δj transitions, for the initial rotational quantum number different from zero, has a simple explanation when magnetic, Δm_j transitions are explicitly considered. The essential features of the Δm_j transition probability distribution are explained using a classical model.

INTRODUCTION

In recent years a wealth of experimental data concerning rotationally inelastic molecule-surface scattering has become available.[1-9] In response to this, a large number of theoretical studies have appeared,[10-30] addressing various aspects of rotational energy transfer in molecule-surface collisions. A very comprehensive review of the research, both experimental and theoretical, in the broad area of gas -usrface interactions and dynamics has been presented recently.[31]

The most intriguing result emerged from a series of experiments by Auerbach and coworkers,[32-34] on the scattering of rotationally cold NO molecules from the Ag(111)surface. They observed that the scattered NO molecules were rotationally polarized, with their final rotational angular momentum $\vec{j}$ preferentially aligned parallel to the surface. Quantum mechanically, this means that, for a given rotational quantum number j, the distribution of the scattered molecules over the set of the rotational projection quantum numbers m_j is non-uniform, the substates with $m_j = 0$ being preferred (taking the surface normal as the quantization axis). The degree of polarization was found to depend strongly on the final rotational quantum number j; both the low and very high j states were essentially depolarized.

The phenomenon of rotational polarization has been studied theoretically in several papers.[34-38] In an interesting paper which examined the dependence of rotational transitions on the initial m_j, McCurdy and coworkers[35] suggested that under certain favourable conditions surface scattering could be utilized to prepare a beam of rotationally polarized molecules (with the final $\vec{j}$ parallel to the surface) which could be subsequently scattered from another surface. Such experiments, if feasible, would certainly produce detailed information about the surfaces involved,[37,38] as well as about the collision dynamics.

In the present work, in anticipation of possible future experiments, we raise the following question: How does the intitial rotational state of the incoming, perfectly rotationally polarized molecule influence the final rotational distribution resulting from the collision with a flat, static surface? To answer this question we employed a twodimensional hard-core ellipsoid-flat surface scattering model developed recertly,[28–30] both in its quantum and classical aspects. In the model, the molecule-surface potential is represented by hard-core ellipsoid and the collisions are assumed to take place in two dimensions. In previous applications to rotationally inelastic molecule-surface collisions[28–30] this model proved capable of yielding both numerically accurate final rotational distributions[28,29] and closed, analytical expressions for the same dominant features present in the final rotational distributions.[30] Treating collisions as occurring in two dimensions actually does not introduce any approximation in the context of the specific problem considered in this work. The molecule which, by assumption, is initially polarized so that $\vec{j}$ is parallel to the surface, after sollision with a flat (or, in reality, weakly corrugated) surface retains the same polarization, i. e. $\vec{j}$ remains parallel to the surface. Hence, the complete collision event is confined to a single plane.

Rotational transitions can be analyzed in two different ways. The molecule before and after collision with the surface may be in a specific magnetic rotational state m_j (i. e. projection of the rotational quantum number j on a fixed axis), in which case we explicitly consider magnetic, Δm_j transitions. Alternatively, and much more commonly, we may be concerned with Δ_j transitions only, where averaging over the initial m_{j_0}'s and summation over the final m_j substates is performed. Molecule collisions with a flat, uncorrugated surface cannot induce Δm_j transitions provided that the surface normal is chosen as the quantization axis. However, when analyzing polarized molecule-flat surface scattering we chose the quantization axis to lie along the rotational angular momentum $\vec{j}$, perpendicular to the surface normal. For the essentially two-dimensional problem at hand, this turned out to be the natural choice of the quantization axis which allowed easy formulation of the quantum scattering equations[28,29] and simple derivation of some analytical results.[30] With respect to this quantization axis, in our two-dimensional world, even for the non-zero quantum number j there are two magnetic substantes $m_j = \pm j$, corresponding to the two possible directions of rotation of the molecule. Given this choice of the quantization axis, Δm_j transitions are possible even for flat surface collisions, since it is clear that collisions with the surface can reverse the direction of the rotational motion. We will demonstrate that the analysis where only the moduli of rotational states, i. e. the rotational quantum number $j = |m_j|$, are observed, is difficult. In contrast, if magnetic Δm_j transitions are considered, a very simple picture emerges which can be readily analyzed.

QUANTUM CALCULATIONS OF Δj AND Δm_j TRANSITIONS AND DISCUSSION

The procedure for calculating rotational transition amplitudes in the quantum 2D hard-core ellipsoid-flat surface scattering was presented earlier.[28,29] The parameters required to characterize a collision system and which enter the scattering equations[28,29] are k_0, the incident molecule wave vector, μ and I, the mass and the moment of inertia of the molecule, respectively (actually, they appear only as the ratio $\varepsilon = \mu/I$), as well as A and B, denoting the major and minor axis of the ellipsoid, respectively.

In the present calculations of rotational transitions, both Δj and Δm_j, we have chosen an ellipsoid with $A = 2.050$ Å and $B = 1.890$ Å, with the ratio $\varepsilon = \mu/l = 3.3178$ Å^{-2}. These parameters describe, within our model, the N_2--surface collision at the collision energy $E_i = 0.30$ eV ($k_0 = 63.4104$ Å^{-1}). The large and small axis values were extracted from the N_2-surface potential used by Voges and Schinke.[22] We first calculated Δj transition probabilities for a series of increasing initial rotational quantum numbers j_0, $j_0 = 0$, 4, 8, 12, 16, 20 and 24. For all the calculations, the collision energy was kept constant, at $E_i = 0.30$ eV. The resultant final rotational distribution probabilities are displayed in Figures 1 and 2.

What is immediately apparent is the complexity of the rotational distributions, especially for lower initial j_0 values, which hardly gives a clue as to the underlying collision dynamics. We also notice two peaks (for $j_0 = 0$ there is only one) centered at low and high final j values respectively, which get more prominent as j_0 increases (Figure 2b). Since the dominant peak for j_0 collision, clearly visible in Figure 1a, is associated with the rotational rainbow, the pattern of transition probabilities for $j_0 \neq 0$, shown in Figures 1b and 2a, b, would suggest that two rotational rainbows are present. One would be tempted to conclude that for $j_0 \neq 0$, the collision mechanism changes from that operating in the $j_0 = 0$ case, and is somehow responsible for the appearance of the two rainbows.

However, a very different, much more illuminating picture emerges when the same collision process is analyzed for Δm_i transition. The Δm_j transition probabilities were calculated when the molecule was initially in a selected m_0 state (without loss of generality we can assume that $m_0 > 0$. If $m_0 < 0$, the transition probabilities are a mirror image of that for $m_0 > 0$, with respect to $m = 0$), and the final states also m states. All the parameters were the same as used for calculating Δj transition probabilities. Calculations were done for $m_0 = 0$, 4, 8, 16 and 24, all at the fixed collision energy $E_i = 0.30$ eV. The results are shown in Figures 3 and 4.

A striking feature of these results is the simplicity of the Δm_j transition probability distributions and the fact that their overall appearance hardly changes with increasing m_0. Increasing m_0 simply shifts the whole distribution towards higher m values leaving intact its basic structure.

From this, the explanation for the two rainbows present in Figures 1 and 2 follows immediately. Since in order to calculate $j_0 \rightarrow j$ transition probability we must sum the transition probabilities from $m_0 \neq \pm j_0$ into $m = \pm j$, the Δm_j transition pattern in Figures 3 and 4, for $m <$ will be superimposed on the transition pattern for $m > 0$. In the $j_0 = 0$ case the two Δm_j rainbow the Δm_j transition pattern in Figures 3 and 4, for $m < 0$ will be superimposed with respect to $m = 0$, as shown in Figure 3a. As j_0 is increased, the Δm_j rainbow peak for $m < 0$ moves towards right along the m-axis (i. e. towards

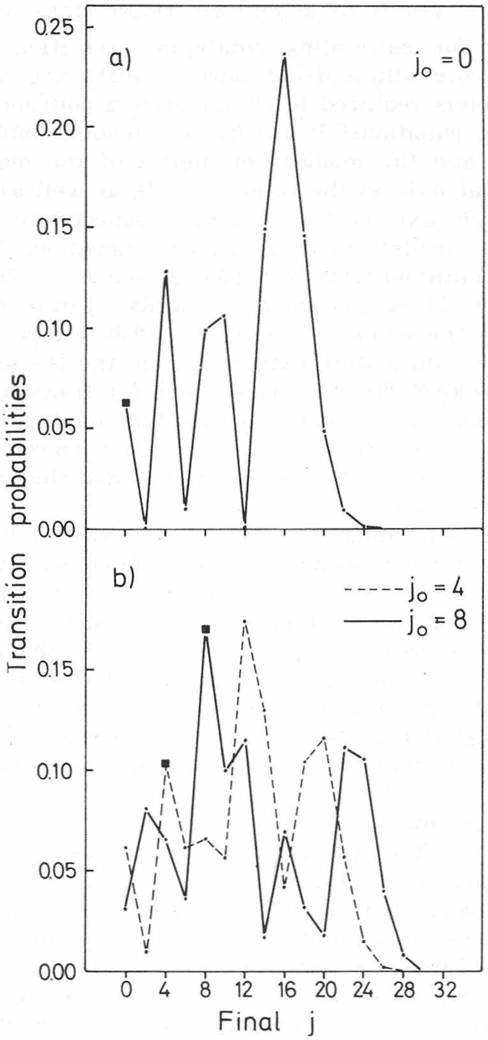

Figure 1. Quantum rotational transition probabilities for $j_o \rightarrow j$, where $j_o = 0$ (a) and $j_o = 4,8$ (b). The two rainbow peaks are not yet well separated. (■) incidate elastic transition.

the positive m values) as can be clearly seen in Figures 3b, c and 4a, b. This will manifest itself in the Δj transitions as one rainbow peak going towards lower j values. As soon as the Δm_j rainbow peak in the $m < 0$ region passes through $m = 0$ (shown in Figure 4b), the trend in Δj transitions will reverse and the Δ_j and Δm_j transition probability patterns become identical. Comparison of Figures 2b and 4b, where $j_0 = 24$ and $m_0 = 24$ rotational distributions, respectively, are shown, illustrates this nicely. Thus, the rainbow peaks which appear in Δ_j transitions have a simple explanation when Δm_j transitions are analyzed.

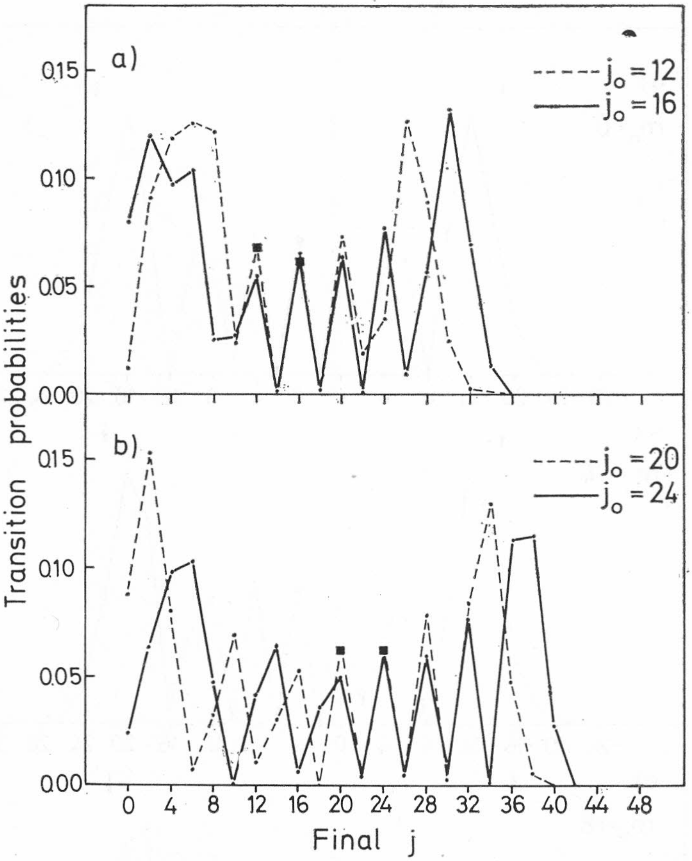

Figure 2. The same as in Figure 1, but for $j_o = 12,16$ (a) and $j_o = 20,24$ (b). Two rainbow peaks are clearly visible, particularly in (b). The origin of two peaks is explained in terms of magnetic transitions (see the text).

The Δm_j transition probability distributions are to a large extent characterized by two features: positions of the two rainbow peaks and the asymmetry of the Δm_j transition pattern with respect to m_0. The asymmetry becomes more pronounced as m_0 increases, which can be seen in Figure 4. In an earlier paper[30] we have developed a purely classical model which completely accounts for these two characteristic features. Expressions have been derived, in a different context, for bounds on the rotational transitoins, excitations as well as deexcitations, from an initial rotational state of molecule (Eqs. (9) and (10) of Ref. 30). The M^+ and M^- states representing the maximally excited and maximally deexcited m states, respectively, which can be reached from m_0 are wiven by

$$M^+ = [j_o + \frac{2\,(A - B)\,k_o}{1 + \varepsilon\,(A - B)^2}\,(1 - (\mathrm{A} - \mathrm{B})\,\frac{j_o \varepsilon}{k_o})]\ \mathrm{Sign}\,(m_o) \tag{1}$$

and

$$M^- = [j_o - \frac{2\,(A - B)\,k_o}{1 + \varepsilon\,(A - B)^2}\,(1 + (\mathrm{A} - \mathrm{B})\,\frac{j_o \varepsilon}{k_o})]\ \mathrm{Sign}\,(m_o) \tag{2}$$

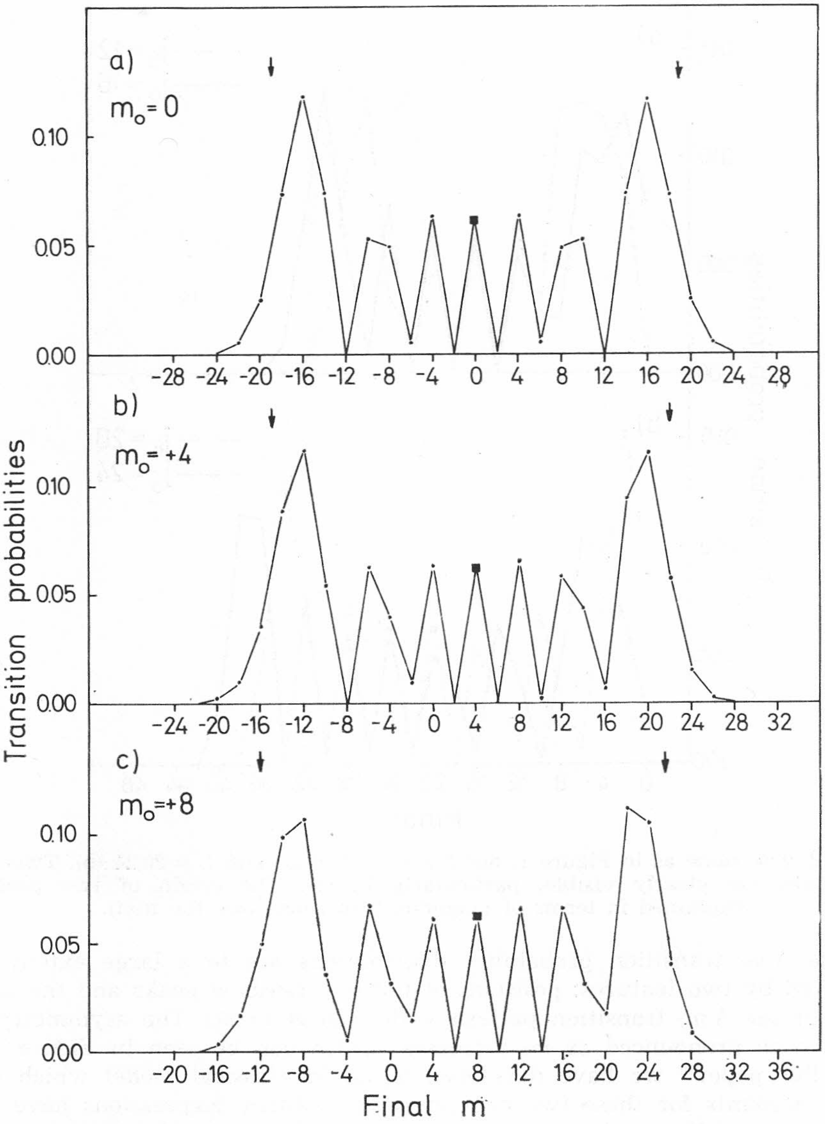

Figure 3. Quantum magnetic rotation transition probabilities for $m_o \rightarrow m$, where $m_o = 0$ (a), $m_o = 4$ (b) and $m_o = 8$ (c). It is evident that the pattern of transition probabilities does not change with m_o, except for the parallel shift. Arrows indicate the position of the rainbow peaks predicted by our model (Eqs. (1) and (2)).

where $j_0 = |m_0|$ and Sign (m_0) gives the sign of m_0. The values of M^+ and M^- states calculated using Eqs. (1) and (2) are marked by arrows in Figures 3 and 4. Evidently, the formulae describe very well the positions of the two Δm_j rainbow peaks, for all m_0 values used in our quantum calculations. Also, the expressions (1) and (2) clearly predict the asymmetry of the Δm_j transition pattern with respect to m_0, i. e. it is evident from the two formulae that

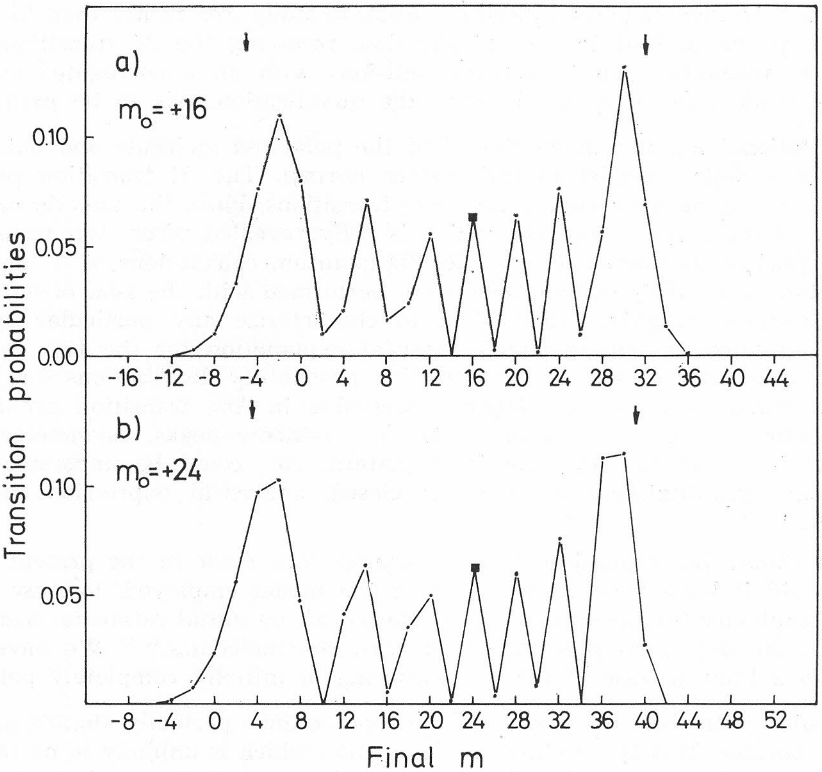

Figure 4. The same as in Figure 3, except $m_o = 16$ (a) and $m_o = 24$ (b). The asymmetry of the transition pattern with respect to m_o is clearly visible. For an explanation of the asymmetry see the text.

$|M^+ - m_0| < |M^- - m_0|$. An interesting consequence of the formulae (1) and (2) is that the separation between the Δm_j magnetic rainbow peaks, $|M^+ - M^-|$, is independent of m_0 and is equal to

$$|M^+ - M^-| = \frac{4\,(A - B)\,k_o}{1 + \varepsilon\,(A - B)^2} \qquad (3)$$

which is confirmed by our quantum calculations (as evident from Figures 3 and 4). The validity of Eqs. (1)—(3) rests, among other things, on the assumption of single molecule-surface collisions.[30] Multiple collisions with the surface modify profoundly the final rotational distribution[29] and then the above equations could not be applied.

CONCLUSIONS

In the present paper we have studied the effect of initial rotation on the final rotational distribution in polarized molecule-(flat) surface scattering. We have shown that in order to get physical insight into the dynamics of this process it is advantageous, indeed essential, to study Δm_j rather than Δj transitions. As emphasized in the Introduction, resolving the Δj transitions into separate magnetic, Δm_j transitions collisions with an uncorrugated surface, was possible only because we chose the quantization axis to be parallel to the rotational angular momentum $\vec{j}$ of the polarized molecule and not, as is commonly done, parallel to the surface normal. The Δj transition pattern, due to averaging over appropriate Δm_j transitions, blurs the underlying simplicity of the collision process, which is fully revealed when Δm_j transitions are explicitly considered. Our model 2D quantum calculations of Δj and Δm_j transition probability distributions were performed with the goal of obtaining some general insights, rather than to characterize any particular system. They provided us with a simple, natural explanation for the two rainbow peaks apparently present in Δj transition probability distributions for $j_o \neq 0$. The dominant features and trends observable in Δm_j transition probability distributions such as positions of the Δm_j rainbow peaks, asymmetry with respect to m_o of the Δm_j transition pattern, etc., could be understood and described quantitatively in terms of closed, analytical expressions derived earlier.[30]

It should be emphasized that no attempt was made in the present work, nor could it have been possible within the model employed, to raise in its full complexity the question of the influence of the initial rotational distribution on the degree of polarization of scattered molecules.[33–35] We have considered a limiting case of surface scattering of initially completely polarized molecules, with their rotational angular momentum $\vec{j}$ perfectly aligned parallel to the surface. This is certainly an idealization which is unlikely to be realized in possible future experiments. However, in our opinion, it is useful and important to obtain a thorough understanding of such a simple process prior to tackling the more complex ones. Given the assumptions inherent to the hard-core ellipsoid- surface scattering model, Eqs. (1)—(3) should give accurate predictions for collision energies relatively high in comparison to any well depth present in the molecule-surface potential.[30]. But, our discussion concerning the interplay between Δm_j and Δj transitions and the conclusions regarding the need for analysis in terms of Δm_j transitions are not affected by such restrictions and should have a broader range of applicability.

REFERENCES

1. J. Cowin, C. F. Yu, S. Sibener, and J. E. Hurst, *J. Chem. Phys.* **75** (1981) 1033.
2. F. Frenkel, J. Häger, W. Krieger, H. Walter, C. T. Campbell, G. Ertl, H. Kuipers, and J. Senger, *Phys. Rev. Lett.* **46** (1981) 152.
3. G. M. McClelland, G. D. Kubiak, H. G. Rennagel, and R. N. Zare, *Phys. Rev. Lett.* **46** (1981) 831.
4. A. W. Kleyn, A. C. Luntz, and D. J. Auerbach, *Phys. Rev. Lett.* **47** (1981) 1169.
5. J. W. Hepburn, F. J. Northrup, G. L. Orgam, J. C. Polanyi, and J. M. Williamson, *Chem. Phys. Lett.* **85** (1982) 127.
6. D. Ettinger, K. Homma, M. Keil, and J. C. Polanyi, *Chem. Phys. Lett.* **87** (1982) 413.
7. J. P. Cowin, C. F. Yu, S. J. Sibener and L. H. Wharton, *J. Chem. Phys.* **79** (1983) 3537.

8. J. Senger, H. Robota, W. Vielhaber, G. Ertl, F. Frenkel, J. Häger, W. Krieger, and H. Walter, *Surface Sci.* **131** (1983) 273.
9. G. D. Kubiak, J. E. Hurst, H. G. Rennagel, G. M. McClelland, and R. N. Zare, *J. Chem. Phys.* **79** (1983) 5163.
10. G. Wolken, *J. Chem. Phys.* **59** (1973) 1159.
11. U. Garibaldi, A. C. Levi, R. Spadacini, and B. E. Tommei, *Surface Sci.* **55** (1976) 46.
12. C. J. Ray and J. M. Bowman, *J. Chem. Phys.* **66** (1977) 1122.
13. R. B. Gerber, A. T. Yinon, Y. Shimoni, and D. J. Kouri, *J. Chem. Phys.* **73** (1980) 4397.
14. J. E. Adams, *Surface Sci.* **97** (1980) 43.
15. D. E. Fitz, A. O. Bawagan, L. H. Beard, D. J. Kouri, and R. B. Gerber, *Chem. Phys. Lett.* **80** (1981) 537.
16. D. E. Fitz, L. H. Beard, and D. J. Kouri, *Chem. Phys.* **59** (1981) 257.
17. R. Schinke, *Chem. Phys. Lett.* **87** (1982) 438.
18. J. M. Bowman and S. Park, *J. Chem. Phys.* **76** (1982) 1168.
19. J. M. Bowman and S. Park, *J. Chem. Phys.* **77** (1982) 5441.
20. R. Schinke, *J. Chem. Phys.* **76** (1982) 2352.
21. J. E. Hurst, G. D. Kupiak, and R. N. Zare, *Chem. Phys. Lett.* **93** (1982) 235.
22. H. Voges and R. Schinke, *Chem. Phys. Lett.* **95** (1983) 221.
23. H. Voges and R. Schinke, *Chem. Phys. Lett.* **100** (1983) 245.
24. J. A. Baker, A. W. Kleyn, and D. J. Auerbach, *Chem. Phys. Lett.* **97** (1983) 9.
25. R. Elber and R. B. Gerber, *J. Chem. Phys.* **79** (1983) 4087.
26. A. M. Richard and A. E. Depristo, *Surface Sci.* **134** (1983) 338.
27. J. C. Polanyi and R. J. Wolf, *Ber. Bunsenges. Physik. Chem.* **86** (1982) 356.
28. Z. Bačić and S. D. Bosanac, *Chem. Phys. Lett.* **105** (1984) 518.
29. Z. Bačić and S. D. Bosanac, *Chem. Phys. Lett.* **103** (1984) 378.
30. Z. Bačić and S. D. Bosanac, *Phys. Rev. A,* in press.
31. J. A. Barker and D. J. Auerbach, *Surface Sci. Reports,* in press.
32. A. C. Luntz, A. W. Kleyn, and D. J. Auerbach, *Phys. Rev.* **B25** (1982) 4273.
33. A. W. Kleyn, A. C. Luntz, and D. J. Auerbach, *Surface Sci.* **117** (1982) 33.
34. A. W. Kleyn, A. C. Luntz, and D. J. Auerbach, to be published.
35. J. G. Landerdale, J. F. McNutt, and C. W. McCurdy, *Chem. Phys. Lett.* **107** (1984) 43.
36. M. H. Alexander, *J. Chem. Phys.* **80** (1984) 3485.
37. T. R. Proctor, D. J. Kouri, and R. B. Gerber, *J. Chem. Phys.* **80** (1984) 3845.
38. T. R. Proctor and D. J. Kouri, *Chem. Phys. Lett.* **106** (1984) 175.

SAŽETAK

Raspršenje polarizirane molekule na glatkoj površini

Z. Bačić i S. D. Bosanac

Istraživano je raspršenje polarizirane molekule na glatkoj površini kada je molekula u početnom stanju pripremljena s rotacijskim kvantnim brojem j paralelnim s površinom. Pokazano je da pojava dvije rotacijske duge u Δj-prijelazima (za početno rotacijsko stanje različito od nule), ima jednostavno objašnjenje kada se uzimaju u obzir Δm-prijelazi. Bitna svojstva Δm-prijelaza objašnjena su klasičnim modelom.