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Features of chemical reactions at vanishing kinetic energy: the presence of internally "hot" reagents

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Abstract. The reactions between vibrationally and rotationally excited H_2 and D_2 molecules and the F atom are analyzed at ultra-low collision energies using the Coupled Channels quantum approach. The aim of this work is to compare the relative efficiency of the reactive scattering event with that of the vibrational or rotational quenching process in the ultra-cold temperature regime in order to establish general trends, possibly amenable to experiments on this or on more complex systems. We have already compared the rotational de-excitation efficiency with the reactive one in the $F + D_2(\nu = 0,\, j = 2) \rightarrow DF + D$ reaction [1] and we have seen in that case that rotational de-excitation is more efficient than reaction when going down to ultra-low energies. We are investigating here the vibrational excitation case when the internal energy of the molecule becomes large enough to be above the classical barrier, and we are also presenting new results for the rotationally hot H_2 partner. We find that, with vibrationally "hot" molecules, the reaction becomes more efficient than the relaxation process, while the relative efficiency of such processes when having rotationally hot molecular partners is much more system-dependent.

PACS. 34.10.+x General theories and models of atomic and molecular collisions and interactions (including statistical theories, transition state, stochastic and trajectory models, etc.) – 34.50.Lf Chemical reactions, energy disposal, and angular distribution, as studied by atomic and molecular beams – 34.20.Mq Potential energy surfaces for collisions

1 Introduction

The dynamics of atoms and molecules at ultra-low kinetic energies (10^{-8}–$1\ \mathrm{cm}^{-1}$) is dominated by quantum effects; at such energies the scattering is essentially determined by the *s*-wave component, for which the relative angular momentum $\mathbf{l}$ is zero. In this regime inelastic and reactive processes may become larger than the elastic scattering because the corresponding cross-sections depend on the inverse of the initial relative velocity. On the experimental side, there are currently various methods employed to produce and trap cold molecules [2–11]: photo-association of ultra-cold atoms, deceleration of molecules through an array of time-varying inhomogeneous electric fields and conversion of an atomic Bose or Fermi gas into a molecular Bose gas by tuning the position of specific Feshbach resonances. In all such cases however, the inelastic collisions taking place in the trap may lead to the conversion of the molecular internal energy into translation energy, hence leading to particle losses.

With the development of techniques for the trapping of molecular gases at ultra-cold temperatures [9,7] and the creation of slowly moving molecular beams [12,13], it may become possible to experimentally explore an unusual collisional regime where the scattering is determined by trajectories with zero relative orbital angular momentum in the entrance channel and where quantum effects such as Feshbach resonances and tunnelling determine the outcome of the collision. Experiments may then become feasible for those reactions whose rates are faster than the decay rate of the the trapped cold molecules due to trap losses. This condition is not trivially satisfied, especially for ground state molecules, because most of the reactions between a neutral molecule and an atom exhibit a barrier along the reaction path that, when the kinetic or internal energy is very low, makes the reaction very slow. Unusually large reaction rate, however, have been predicted for neutral reactions such as $F + H_2 \rightarrow HF + H$ [14] and, to a lesser extent, $F + D_2 \rightarrow DF + D$ [15] and attributed to the large tunneling rate of the light atom through the activation barrier. On the other hand, one may speculate that an initially excited molecule could have enough internal energy to overcome the reaction barrier even when the kinetic energy is extremely low, but that it may not be easy to trap such species because inelastic deactivation (quenching) can be very efficient. We have already shown [1], for example, that for the $F + D_2(\nu = 0, j = 2)$ system the rotational quenching of the rotationally

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excited reagents is more efficient than the relevant reaction and may cause severe trap losses before the reaction takes place.

In the present work we will show that, for the two systems analyzed here, the reaction of vibrationally excited molecules remains more efficient than vibrational quenching, although slower than the reaction involving ground state molecules. In addition, we will see that rotational de-excitation processes are even more effective and can therefore compete with reactions.

2 Reactive calculations and results

The calculations have been performed using the `abc` program of Skouteris et al. [16] and the Stark and Werner potential energy surface [17]. The integration range was quite large in order to obtain converged reactive cross-section to 1% and elastic cross-sections to 10%. The maximum hyperradius value used for the asymptotic condition was 250 a.u. The step of the propagation was 0.005 a.u. For vibrationally excited molecules, we have included all the vibrational and rotational channels of both products and reactants up to 4.0 and 4.5 eV of energy for the reaction with H_2 and D_2 respectively (energies are measured with respect to the bottom of the reactant channel). We have, however, limited the maximum allowed value of the molecular rotational quantum number to $j_{max} = 12$ for the reaction with H_2 and $j_{max} = 22$ for that with D_2. The total number of channels included in the coupled equations was 289 for H_2 and 739 for D_2. Since the initial molecule, although vibrationally excited, is in the $j = 0$ state we have performed only zero total angular momentum calculation in order to obtain the s-wave component that is the only contribution below 10^{-5} eV of collision energy. For rotationally excited molecules we have used the same basis already used in references [14,15], but we have performed calculations with total angular momentum value of $J = 2$ to correctly include the $l = 0$ component for an initial molecule in the $j = 2$ state. In this case the S-matrix elements expressed in the helicity representation are labelled by different values of the projection of the total angular momentum onto the Body-Fixed axis (k see Ref. [16]). We have summed these contributions in order to obtain initial state-resolved cross-sections.

2.1 Vibrationally "hot" reagents

Here we present two set of calculations with the molecule initially in the vibrationally excited state $\nu = 1$. We begin by looking at the Minimum Energy Path (MEP) of the reaction reported as a solid line in Figure 1 and calculated using the ABCRATE [18] program. The "classical" barrier is of 0.083 eV. It is possible to include the quantum effect due to the initial vibrational state of the molecules by computing the vibrationally adiabatic potential (VAP) defined as

$$V_\nu(s) = V_{MEP}(s) + \varepsilon_\nu(s) \qquad (1)$$

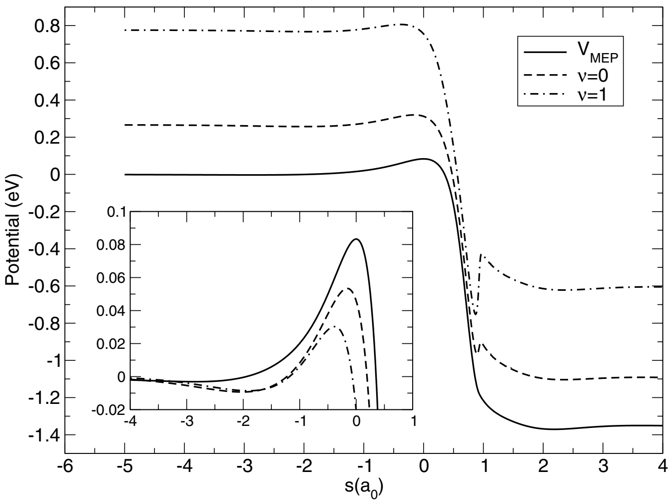

Fig. 1. Minimum energy path and vibrationally adiabatic potentials for the reaction $F + H_2 \rightarrow HF + H$.

where s is the reaction coordinate and ε_ν is the adiabatic vibrational energy of the bound state transverse to the MEP calculated using the Morse I approximation [18]. The adiabatic vibrational energy coincides with the vibrational energy content of the reagents when the system is in the reactants arrangement and in equation (1) $s \rightarrow -\infty$. It then smoothly varies along the reaction coordinate and becomes the energy of the vibrational "mode" transverse to the reaction coordinate in the transition state.

The two VAP for $\nu = 0$ and $\nu = 1$ are also reported in Figure 1 relative to the bottom of the potential well in the entrance channel. We see that including the zero point energy effect lowers the barrier to 0.058 eV (for comparison, see for example the value given in Ref. [19]) and that, for a vibrationally excited molecule, the adiabatic barrier is of about 0.030 eV. The relative height of the three barriers is directly compared in the inset of Figure 1 where the corresponding asymptotic vibrational energies have been subtracted. The VAP's reported in Figure 1 have been calculated for the $F + H_2$ system. In the case of D_2 there are very little changes in the qualitative features of the potentials: the adiabatic barriers become 0.063 and 0.043 eV for $\nu = 0$ and $\nu = 1$ molecules respectively. As we shall see below, the energy range which we are interested in is well below the adiabatic barriers even for molecules in the $\nu = 1$ state. Thus, chemical reactions in this regime are still taking place by the tunneling of H or D atoms.

The results for $F + H_2(\nu = 1)$ and $F + D_2(\nu = 1)$ are presented in Figure 2. During the collision we can have simple elastic scattering, reaction process or vibrational quenching: we therefore show the cross-sections for all three possible processes. The vibrational quenching and reactive cross-section have been obtained by summing over all the final ro-vibrational states. In both cases, reaction is seen to be faster than vibrational quenching, although the difference between the two inelastic cross-sections is not very large: around a factor of 7 for H_2 and 5 for D_2. Moreover we expect that the efficiency of vibrational quenching processes should increase when moving to higher excited

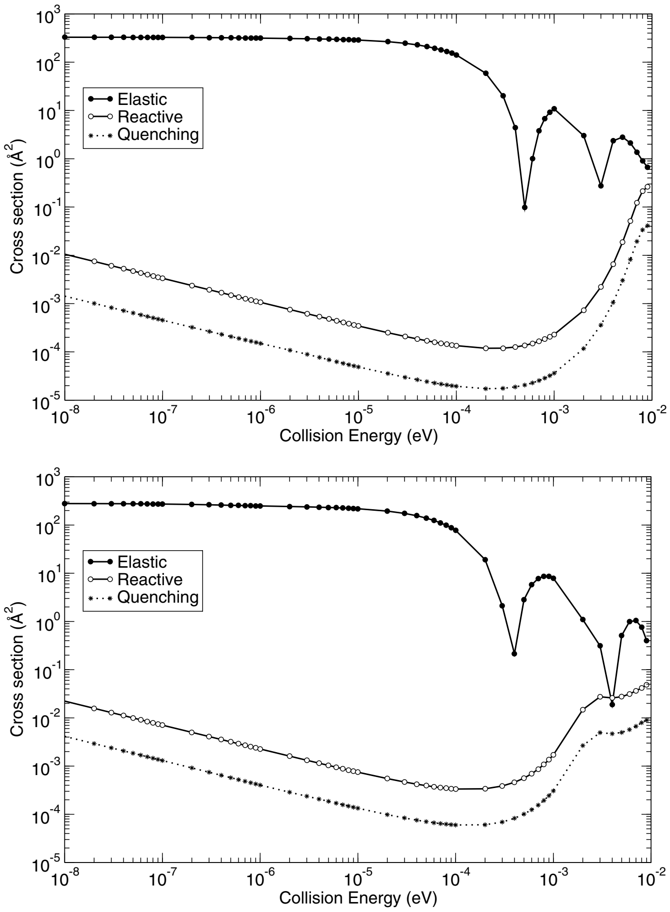

Fig. 2. Vibrational de-excitation, total reaction and elastic cross-section for $F + H_2 \rightarrow HF + H$ (upper panel) and for $F + D_2 \rightarrow DF + D$ (lower panel).

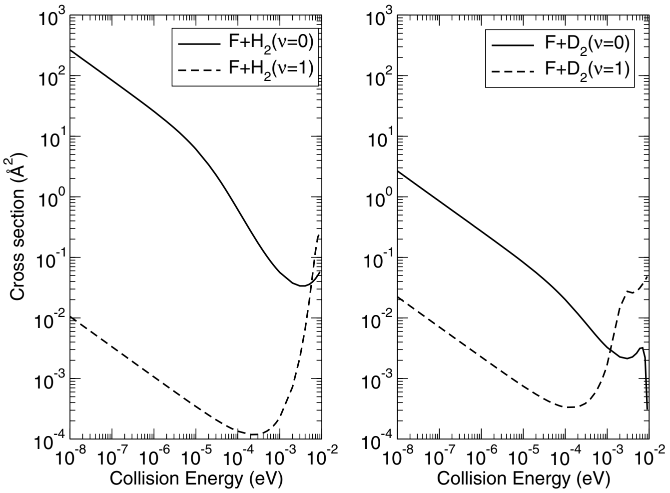

Fig. 3. Total cumulative cross-sections for the reaction $F + X_2(\nu = 0, 1) \rightarrow FX + X$ with $X = H$ (left) and $X = D$ (right).

states (see for example Ref. [20]) and this may thus lead to situations in which the vibrational quenching becomes dominant. Unfortunately it turned out to be very difficult to numerically test the latter situations because of the impossibility of finding converged (and size manageable) asymptotic expansions with which to carry out calculations with molecules in higher ν states.

It is interesting to notice at this point that the vibrational excitation reduces significantly the reaction cross-section: this reduction is much more evident in the case of H_2. In Figure 3 we report a comparison between the cumulative reactive cross-sections obtained from the calculations with the initial molecule in $\nu = 0$ [1,14] and $\nu = 1$. In the left panel we notice a dramatic depletion of the reactive cross-section for the H_2 system. This large difference is probably due to the fact that in the case of vibrationally excited molecule a specific favourable coupling with a virtual state in the entrance channel disappears: it had already been discussed by us [21] that, due to such a feature, the cross-section for $F + H_2(\nu = 0)$ was unexpectedly large. However, also in the case of D_2, where the effect of the virtual state is absent, we still notice here a significant reduction of the reaction cross-section when reacting with vibrationally excited molecules. This unexpected behavior only occurs when the reaction proceeds by tunneling below the barrier, as can be seen clearly from Figure 3 where the $\nu = 1$ cross-section is seen to rapidly overcome the $\nu = 0$ cross-section just above 10^{-3} eV for both reactions. Since there is almost no difference in the density of states available to molecules in the $\nu = 0$ and $\nu = 1$ states, presumably the effect depends on the magnitude of the couplings that transfer the reactant molecule from its initial ν state to all the product states. It therefore follows that the calculations reported here show that, for some systems, it might be possible to observe even experimentally initial state-selected chemical reactivity in traps because the loss rate would be dominated by chemical reactions and not by inelastic de-excitation (quenching).

Another effect of vibrational excitation is to shift the final rotational population of the XF molecule towards larger j' values. In Figure 4 we show the normalized rotational populations calculated as

$$P(\nu', j') = \frac{|S(\nu, j = 0 \rightarrow \nu', j')|^2}{\sum_{j'} |S(\nu, j = 0 \rightarrow \nu', j')|^2} \quad (2)$$

where we have chosen $\nu' = 2$ for HF and $\nu' = 3$ for DF because they are the most populated vibrational levels in the reactions from $\nu = 0$. However, the changes in the rotational distributions are seen not to be very large, the main difference being the shift to higher j' values in the products and the lack of population for the small-j' states of the products.

2.2 Rotationally "hot" reagents

We now analyze the case in which the reactant molecules are rotationally excited and, in particular, in the $j = 2$ state of their ground vibrational manifold. Two exothermic processes are therefore possible: either rotational quenching or reaction. We have already calculated the

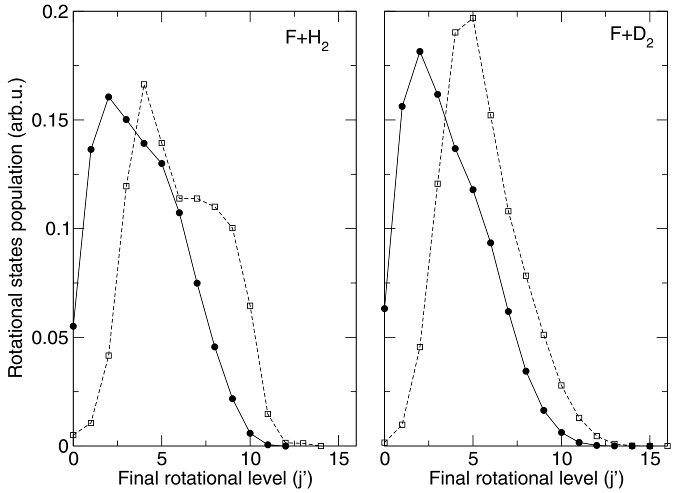

Fig. 4. Left: final rotational populations of the FH molecule in the $F + H_2(\nu, j = 0) \rightarrow HF(\nu' = 2, j') + H$ reaction. Right: final rotational populations of the FD molecule in the $F + D_2(\nu, j = 0) \rightarrow DF(\nu' = 3, j') + D$ reaction. Black circles correspond to $\nu = 0$, white squares to $\nu = 1$.

cross section for the two processes in the reaction $F + D_2(\nu = 0, j = 2) \rightarrow FD + D$ in reference [1] and we have seen that rotational quenching is dominant at ultralow energies. We report here a slightly improved version of those calculations (in terms of asymptotic basis and propagator parameters) together with new calculations for the hydrogen reaction $F + H_2(\nu = 0, j = 2) \rightarrow FH + H$.

As in the preceding section, we begin by showing (in Fig. 5) the cross-sections for the three possible processes. As we can see there, the relative efficiency of reaction against quenching depends now on the system considered. We confirm, in fact, that for $F + D_2$ rotational quenching is faster than reaction[1], but we see instead that in the case H_2, its reaction cross-section remains larger than quenching. The latter situation is due to the fact that reaction in the case of H_2 proceeds via an unusually large cross-section for reasons that we have already mentioned in the previous section and in our earlier work [21].

Drawing general conclusions about rotationally "hot" molecules is more difficult than in the case of the vibrational channels. Here the two systems show rather different behavior and, although quenching is more efficient for D_2 than for H_2 (possibly due also to the smaller energetic gap between the rotational states of the former) the ratio of its cross-section and that of the reactive process is not very large. Moreover the results obtained by Balakrishnan and Dalgarno [22] in the F + HD system further show that reaction is more efficient than quenching. We also have to consider that in the case of the H_2 molecule the rotational coupling is rather small because of the small angular anisotropy of its interaction with atomic partners.

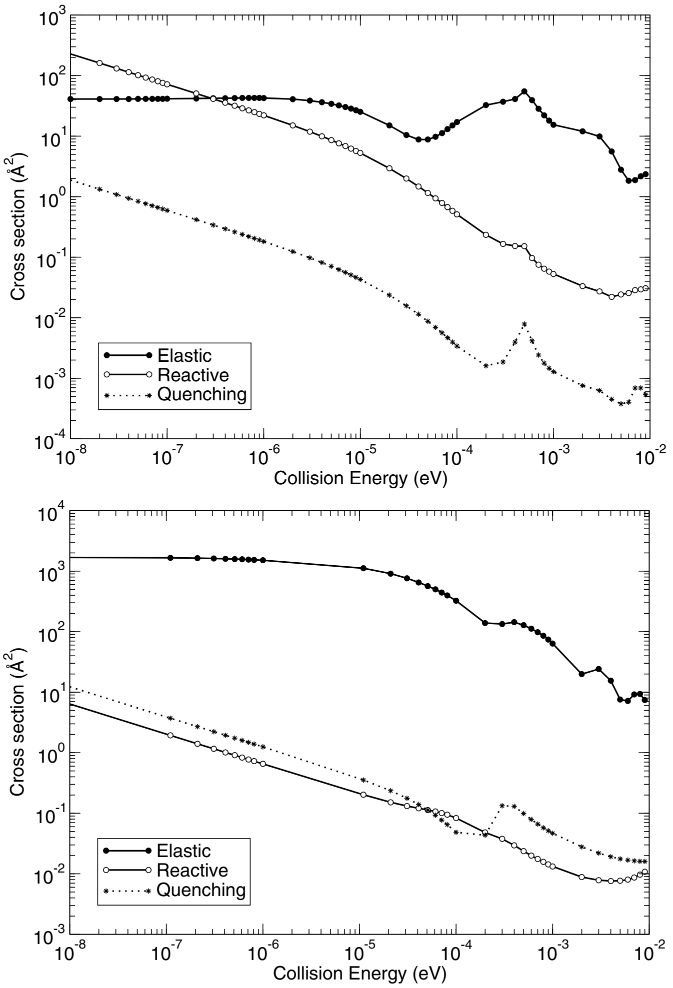

Fig. 5. Rotational de-excitation, total reaction and elastic cross-section for $F + H_2 \rightarrow HF + H$ (upper panel) and for $F + D_2 \rightarrow DF + D$ (lower panel).

As we did in the preceding section we further report in Figure 6 a comparison between the reactive and elastic cross-sections obtained when involving either ground state and "hot" molecular reagents. In the case of H_2 (left panels) the dynamics seems to remain quite similar in the two cases: both the reactive and the elastic cross-sections show very small differences within each other. The enhancing effect of the virtual state [21] is there also in the case of $j = 2$ molecules as confirmed by the fact that the elastic cross-section shows the same kind of Ramsauer minimum feature discussed in our earlier work [21], although in the present case of $j = 2$ it is somewhat washed out because of the sum over the different components corresponding to different values of the angular momentum projection k that contribute to the cross-section [16]. In the case of D_2 the differences are slightly more marked and the elastic cross-section is now much larger for $j = 2$ reagents while the reaction is only slightly less efficient. Also in this case the main features of the scattering process remain almost unchanged when going from "cold" to "hot" reagents.

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[1] The results shown here are different from those presented in reference [1] because here we have summed all the initial k contributions while there we limited ourselves to the $k = 0$ component of the scattering.

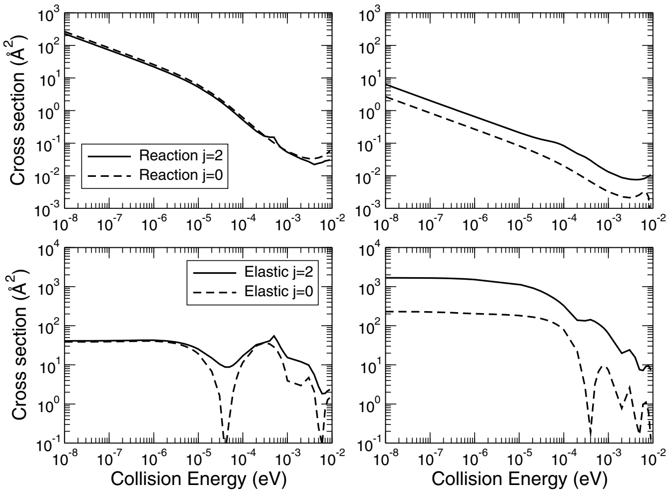

Fig. 6. Total cumulative cross-section (upper panels) and elastic one (lower panels) for the reaction $F + X_2(\nu = 0, 1) \rightarrow FX + X$ with $X = H$ (left) and $X = D$ (right).

3 Conclusions

The numerical "experiments" shown here present for the first time the low-energy reactive behavior of vibrationally and rotationally excited molecules for a well known benchmark chemical reaction. We have seen that in each of the two cases examined vibrational quenching is less favoured with respect to reaction despite the presence of adiabatic activation barriers of around 400 K: it may thus be possible to generalize this behavior to other neutral reactions with small activation barriers by drawing on the present experience. We expect, however that a larger degree of vibrational excitation might lead to larger quenching cross sections, although to actually find the crossover region would require additional calculations. In the case of rotationally "hot" partners we have seen different results in the two cases, but in general, rotational quenching should be more efficient with respect to the vibrational one and in cases, like D_2, it may overcome the reaction process. We should stress here that the present system shows a very small angular anisotropy and hence very small rotational dynamical couplings.

We have also compared the changes in reaction efficiency when going from "cold" to "hot" molecular partners: unexpectedly, vibrationally excited molecules turn out to be much less efficient in reaction. This behavior seems not to depend on kinematic effect (due to the low kinetic energy in the entrance arrangement), nor on density of states in the product arrangements, but it is probably due to the lack of efficient vibrational couplings in the product arrangements. On the other hand, we have also seen that a small degree of pure rotational excitation in reagents molecule does not alter significantly the dynamical picture with respect to ground state molecules (see especially the results for the $F + H_2$ reaction). In this last reaction we have, indeed, seen that also for $j = 2$ the Ramsauer minimum already discussed by us for the case of ground state reactants [21] can still be detected in the elastic cross-section.

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References

1. E. Bodo, F.A. Gianturco, A. Dalgarno, J. Phys. B **35**, 2391 (2002)
2. B.G. Levi, Phys. Today **53**, 46 (2000)
3. R. Wynar, R.S. Freeland, D.J. Han, C. Ryu, D.J. Heinzen, Science **287**, 1016 (2000)
4. G. Meijer, Chem. Phys. Chem. **3**, 495 (2002)
5. M. Greiner, C.A. Regal, D.S. Jin, Nature **426**, 537 (2003)
6. J. Herbig, T. Kraemer, M. Mark, T. Weber, C. Chin, H.-C. Nägerl, R. Grimm, Science **301**, 1510 (2003)
7. S. Jochim, M. Bartenstein, A. Altmeyer, G. Hendl, S. Riedl, C. Chin, J.D. Denshlag, R. Grimm, Science **302**, 2101 (2003)
8. P. Pillet, N. Vanhaecke, C. Lisdat, D. Comparat, O. Dulieu, A. Crubellier, F. Masnou-Seeuws, Phys. Scripta **T105**, 7 (2003)
9. K.E. Strecker, G.B. Partridge, R.G. Hulet, Phys. Rev. Lett. **91**, 80406 (2003)
10. K. Xu, T. Makaiyama, J.R. Abo-Shaeer, J.K. Chin, D.E. Miller, W. Ketterle, Phys. Rev. Lett. **91**, 210402 (2003)
11. M.W. Zwierlein, C.A. Stan, C.H. Schunck, S.M.F. Raupach, S. Gupta, Z. Hadzibabic, W. Ketterle, Phys. Rev. Lett. **91**, 250401 (2003)
12. L.H. Bethlem, G. Berden, G. Meijer, Phys. Rev. Lett. **83**, 1558 (1999)
13. F.M.H. Crompvoets, R.T. Jongma, H.L. Bethlem, A.J.A. van Roij, G. Meijer, Phys. Rev. Lett. **89**, 93004 (2002)
14. N. Balakrishnan, A. Dalgarno, Chem. Phys. Lett. **341**, 652 (2001)
15. E. Bodo, F.A. Gianturco, A. Dalgarno, J. Chem. Phys. **116**, 9222 (2002)
16. D. Skouteris, J.F. Castillo, D.E. Manolopoulos, Comp. Phys. Comm. **133**, 128 (2000)
17. K. Stark, H.-J. Werner, J. Chem. Phys. **104**, 6515 (1996)
18. B.C. Garrett, G.C. Lynch, T.C. Allison, D.G. Truhlar, Comp. Phys. Comm. **109**, 47 (1998)
19. T. Takayanagi, Y. Kurosaki, Chem. Phys. Lett. **286**, 35 (1998)
20. N. Balakrishan, R.C. Forrey, A. Dalgarno, Phys. Rev. Lett. **80**, 3224 (1998)
21. E. Bodo, N. Balakrishnan, A. Dalgarno, F.A. Gianturco, Phys. Rev. Lett. (in press, 2004)
22. N. Balakrishnan, A. Dalgarno, J. Phys. Chem. A **107**, 7101 (2003)