Trapping laser excitation during collisions limits the lifetime of ultracold molecules

Arthur Christianen,1 Martin W. Zwierlein,2 Gerrit C. Groenenboom,1 and Tijs Karman3,4

1Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands
2MIT-Harvard Center for Ultracold Atoms, Research Laboratory of Electronics, and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
3HAMP, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, 02138, USA

The lifetime of nonreactive ultracold bialkali gases was conjectured to be limited by sticky collisions amplifying three-body loss. We show that the sticking times were previously overestimated and do not support this hypothesis. We find that electronic excitation of NaK+NaK collision complexes by the trapping laser leads to the experimentally observed two-body loss. We calculate the excitation rate with a quasiclassical, statistical model employing ab initio potentials and transition dipole moments. Using longer laser wavelengths or repulsive box potentials may suppress the losses.

Ultrasound dipolar gases have exciting applications across physics and chemistry [1, 2]. They can be used for high-precision measurements that challenge the standard model [3, 4], to model or simulate quantum many-body physics [5, 7], and to study and control chemical reactions [8, 9]. There are also promising schemes for quantum computation using ultrasound dipolar gases [10–12].

The first ultracold dipolar molecules in their absolute rovibronic and hyperfine ground state were realized by Ospelkaus et al. [13]. The KRb molecules used were reactive [9, 14], which limits the lifetime of these ultracold gases. To avoid losses due to chemical reactions, several groups realized nonreactive ultracold dipolar gases of the bosonic 87Rb-133Cs [15, 16, 23Na-87Rb [17] and the fermionic 23Na-40K [18, 19]. However, losses were still observed at about the same rate that would be expected of reactive molecules [20, 22]. In all of these experiments, the lifetime of the gas in the crossed optical dipole trap was limited to a few seconds [15] or less [15, 17]. Preventing this loss is of crucial importance for realizing higher molecular densities required for loading optical lattices and to improve the coherence time of ultracold molecules [23].

The loss mechanism in these nonreactive gases is not yet understood, but there are strong indications that the loss is caused by ultracold molecular collisions, which have been studied extensively in the literature [24]. Mayle et al. [25, 26] proposed that the loss mechanism may be due to “sticky collisions”, the formation of long-lived collision complexes. What actually happens to these complexes that causes loss of molecules from the trap is unknown and the subject of this paper. We show that laser excitation of these complexes may explain the losses in the experiments.

Mayle et al. [25, 26] propose a procedure to calculate the sticking time of a collision complex by calculating the density of states. Rice-Ramsperger-Kassel-Marcus (RRKM) theory [27] relates the sticking time \( \tau_{\text{stick}} \) of the collision to the density of states (DOS, \( \rho \))

\[
\tau_{\text{stick}} = 2\pi \hbar \rho.
\]  

In the accompanying paper [28], we show that the sticking times estimated previously were two to three orders of magnitude too large due to an error in the DOS calculation. A quasiclassical equation to accurately calculate the DOS for arbitrary potentials is found:

\[
\rho = \frac{g_{N J \mu} 8 N \pi^2 \hbar^3 C_{Nm}(2J + 1)}{\Gamma(Nm)} \int G(q) |E - V(q)|^{N / 2 - 1} dq.
\]  

Here, \( E \) is the total energy in the system, \( J \) is the total angular momentum quantum number, \( \mu \) is the parity and \( V(q) \) is the potential energy as a function of the Jacobi coordinates of the complex \( q = (R, r_1, r_2, \theta_1, \theta_2, \phi) \): the intermolecular distance \( R \), the bond lengths \( r_1, r_2 \), the polar angles, \( \theta_1, \theta_2 \), and the dihedral angle, \( \phi \) (see Ref. [29]). The complex has \( D = 6 \) internal degrees of freedom. The constant \( C_{Nm} \), parity factor \( g_{N J \mu} \), and geometry factor \( G(q) \) are defined in the accompanying paper [28]. The factor \( g_{N J \mu} \) is 1/2 in this case.

We use Eq. (2) and the recently constructed, accurate potential energy surface (PES) [29] to calculate the DOS for the NaK+NaK system. These calculations result in a DOS of 0.37 \( \mu K^{-1} \) (for \( J = 1 \)) and a sticking time of about 18 \( \mu s \). We showed that this lifetime is not long enough for complex-diatom collisions to explain the experimental losses [28].

In this paper, we show that the excitation of collision complexes by the trapping laser can explain the losses observed experimentally. In typical experiments, the diatoms are confined using a crossed optical dipole trap with lasers far red detuned (1064 nm [15, 18, 20, 23] or 1550 nm [16, 19, 30]) from the molecular \( X^1 \Sigma^+ \rightarrow A^1 \Sigma^+ \) transition. However, the electronic excitation energies of the complex differ from those of the individual molecules and depend on the nuclear geometry of the complex. This means that even though the laser is red detuned for the diatoms, the laser may electronically excite the collision complex.

Figure 1 shows the ground state and low-lying singlet excited states of NaK+NaK as a function of the intermolecular distance for a planar configuration of \( C_{2h} \) symmetry. Colors correspond to the different irreducible rep-
The third excited state of the complex correlates to both the ground state energy curve plus the photon energy \( R \) points were calculated over the entire range of \( R \) with intervals of 0.5 \( a_0 \). The dashed line indicates the ground state energy curve plus the photon energy \( h\omega \) of a 1064 nm laser. With this geometry, the complex has a \( C_{2h} \) symmetry. The colors in the graph correspond to the irreducible representations of the states, blue for \( A_g \), green for \( A_u \), red for \( B_u \), and cyan for \( B_g \). Absorption. We see that the excited-state potentials are more strongly bound than the ground-state potential, and the excited potentials cross the blue dashed line in Fig. 1.

We calculate the expectation value of \( b_{i \rightarrow f}(q, \omega) \) over the accessible phase space as a function of \( \omega \). We assume the linewidth of the transition is small compared to the variation of the energy gap between the ground state and the excited state with geometry, \( E_{\text{gap}}(q) \), and replace \( g(q, \omega) \) by a delta function,

\[
\langle b_{i \rightarrow f}(q, \omega) \rangle_g = \frac{gN_J}{h^2} \frac{8s^{3+} \frac{2}{J} h^3 C_{\text{symm}}(2J + 1)}{3e_0^2 h^2 \Gamma(\frac{J}{2}) \rho} \int dq G(q) \left[ E_{\text{tot}}(y) - V(y) \right]^{J-1} \mu_{i \rightarrow f}(q) \delta \left( \frac{E_{\text{gap}}(q)}{h} - \omega \right).
\]

The linewidth of the laser is also very small with respect to the variation of the excitation energy as a function of the geometry, such that \( dI/d\omega \) can be replaced by \( I_{\text{tot}}(\omega_{\text{laser}} - \omega) \). We then sum over the electronic final states \( f \) to obtain

\[
\frac{dn_c}{dt} = -n_c \sum_i \Gamma_{i \rightarrow f} = -n_c \sum_i \frac{I_{\text{tot}}(b_{i \rightarrow f}(\omega_{\text{laser}}))}{c},
\]

where \( \Gamma_{i \rightarrow f} \) is the excitation rate from state \( i \) to \( f \). We define \( \Gamma_{\text{laser}} = \sum_i \Gamma_{i \rightarrow f} \) and \( t_{\text{laser}} = \Gamma_{\text{laser}}^{-1} \).

Before evaluating Eq. (6), we first qualitatively explore the properties of the TDM between the ground state and the low-lying excited states by again considering the one-dimensional cut for the \( C_{2h} \) configuration. Due to symmetry, only \( A_u \) and \( B_u \) states have nonzero TDMs with the ground state. We show the TDMs of

\[
W_{i \rightarrow f}(q) = -\int d\omega \frac{b_{i \rightarrow f}(q, \omega)n}{c} \frac{dI}{d\omega},
\]

where \( n \) is the particle density and \( dI/d\omega \) is the spectral irradiance of the laser. The coefficient \( b_{i \rightarrow f} \) is given by

\[
b_{i \rightarrow f}(q, \omega) = \frac{\pi}{3e_0 h^2} \mu_{i \rightarrow f}(q)^2 g(q, \omega),
\]

representations of the electronic states. The potentials were calculated \textit{ab initio} using internally contracted multireference configuration interaction with MOLPRO [31], as described in more detail in the Supplement [32]. The lowest two excited states correlate asymptotically to \( X^1\Sigma^+ \rightarrow A^1\Sigma^+ \) excitations of one of the NaK molecules. The third excited state of the complex correlates to both molecules excited to \( a^3\Sigma^+ \). Above that, we find excited states correlating to single \( X^1\Sigma^+ \rightarrow B^1\Pi \) excitations, as well as simultaneous excitation of one molecule to \( a^3\Sigma^+ \) and the other to \( b^3\Pi \). These highest two thresholds are nearly degenerate and their order depends on the monomer bond lengths. Higher excited states correlating to Na(S \( \rightarrow P \)) transitions and more highly excited triplet states exist, but do not contribute to the absorption. We see that the excited-state potentials are more strongly bound than the ground-state potential, e.g., the first excited state potential has a well depth in the order of 12 000 cm\(^{-1}\) compared to the well depth of 4534 cm\(^{-1}\) of the ground-state potential [29]. The dashed line shows the ground-state potential shifted up by 1064 nm. This curve crosses four excited-state potentials in the region where the ground-state potential is attractive, indicating that these excited states can be reached. Furthermore, strong transition dipole moments (TDMs) to these excited states exists as the NaK \( A^1\Sigma^+ \) and \( B^1\Pi \) excited states correlate to parallel and perpendicular dipole-allowed K(S \( \rightarrow P \)) transitions.

This establishes that the energies of the excited states are low enough for trapping-laser-induced electronic transitions of collision complexes to occur. Next, we calculate the rates of these transitions to determine whether these transitions occur within the lifetime of a complex.

The rate equation for laser excitation of the complex for a frozen geometry, \( q \), from discrete state \( i \) to \( f \) is given by [33]

\[
W_{i \rightarrow f}(q) = -\int d\omega \frac{b_{i \rightarrow f}(q, \omega)n}{c} \frac{dI}{d\omega},
\]

FIG. 1: A one-dimensional cut of the NaK+NaK PESs for the ground state and several excited states. The geometry is \( r_1 = r_2 = 6.9 \) \( a_0 \), \( \theta_1 = 3\pi/4 \), \( \theta_2 = \pi/4 \), \( \phi = \pi \). \textit{Ab initio} points were calculated over the entire range of \( R \) with intervals of 0.5 \( a_0 \). The dashed line indicates the ground state energy curve plus the photon energy \( h\omega \) of a 1064 nm laser. With this geometry, the complex has a \( C_{2h} \) symmetry. The colors in the graph correspond to the irreducible representations of the states, blue for \( A_g \), green for \( A_u \), red for \( B_u \), and cyan for \( B_g \).
the two lower-lying $B_u$ states in Fig. 2. At long range, the $1B_u$ state corresponds to $(|AX⟩−|XA⟩)/√2$, the anti-symmetric combination of $X^1Σ^+ → A^1Σ^+$ excitations in either molecule. The $A$ excited state correlates to $K(S → P)$ transitions. The molecular TDMs add constructively such that the $1B_u$ linestrength approaches twice the linestrength of the $S → P$ transition of the $K$ atom, $μ^2 ∼ 17(ea_0)^2$. Asymptotically, the $2B_u$ state corresponds to $a^3Σ^+ + b^5Π$, which has zero TDM with the ground state. For $R < 20 a_0$, these states mix such that the $1B_u$ TDM decreases and the $2B_u$ TDM increases, but the sum remains nearly constant. At yet shorter distances, $R < 10 a_0$, short-range effects decrease all TDMs. The more highly excited states can be reached energetically only at very short range, where the TDMs drop substantially, such that the lowest three excited states dominate the excitation rate. In what follows, we include only these three excited states.

The evaluation of Eq. (5) requires global PESs and TDM surfaces, rather than the one-dimensional cuts discussed above. For the ground state, we use the GP9 PES from Ref. [20]. New PESs for the lowest three excited states are constructed to describe the gaps between the electronic energy levels. We also construct TDM surfaces for these excited states, and fit all surfaces using our machine-learning fitting method [29]. The details are described in the Supplementary Information [32].

For geometries with lower symmetry, the excited states exhibit many avoided crossings and conical intersections that complicate the electronic structure calculations. Conical intersections are expected to occur, e.g., from the many crossings observed in Fig. 2 and because the energetic ordering of electronic states switches between arrangements; the $a^3Σ^+ + a^3Σ^+$ state is the third excited state in the NaK+NaK arrangement, but the second excited state for Na$_2$+K$_2$. Intersections occur at intermediate geometries. Near conical intersections, the TDM and potential energy vary rapidly with nuclear geometry, and the individual surfaces are difficult to fit accurately. However, we are interested in the laser-excitation rate, which is computed as a phase-space average summed over electronically excited states, and is less sensitive to the quality of the fits for individual electronic states.

The global TDM surfaces constructed here exhibit features similar to those observed at the $C_{2v}$ symmetric configuration. At long range, the excited states have large TDMs due to their $K(S → P)$ character. For lower-symmetry configurations, the lowest three excited states mix strongly and the linestrength distributes over the excited states, such that the individual squared TDMs vary with geometry, but the total remains approximately constant. At yet shorter range, the total TDM decreases.

Figure 3 shows the laser excitation rate as a function of the frequency at a trap depth of 10 µK, calculated using the dynamic polarizabilities from Ref. [35]. The colored lines indicate the laser transition rates to the individual excited states, the black line indicates the total. The grey shaded area indicates the error margin, which is estimated as described in the Supplement [32]. The vertical dotted lines indicate wavelengths of 10.6 µm, 1550 nm, and 1064 nm lasers.

At 1064 nm, the loss rate is $Γ_{laser} = 3.3 \, µs^{-1}$, which corresponds to a lifetime for...
The estimated lifetime of the complex with respect to complex-molecule collisions $\tau_{3b} = 1/[n(0)k_{3b}]$, where $n(0)$ is the initial molecular density and $k_{3b}$ the molecule-complex collision rate. At 1064 nm and 1550 nm, in the typical range of experimental intensities, we find laser excitation leads to effective two-body loss, limited by the formation of collision complexes, and is insensitive to small changes in wavelength and intensity. For a 10 µm wavelength, however, the lifetime of the molecules becomes orders of magnitude larger and strongly intensity-dependent. Changing the trapping laser wavelength to 10 µm emerges as a straightforward way to strongly reduce the losses. However, even at this wavelength the laser excitation of collision complexes is dominant over sticking-amplified three-body loss.

Possibilities for reducing collision complexes is dominant over sticking-amplified three-body loss.

1. Box potentials. Rather than switching to very long wavelengths, a promising avenue may be to use shorter wavelengths to realize repulsive potential walls of blue-detuned trapping light [36], such that molecules are trapped between them in the dark. Such uniform box potentials have been realized for ultracold atoms, for both Bose-Einstein condensates [37] and Fermi gases [38].

2. Preventing molecular collisions. If molecular collisions are suppressed, fewer collision complexes are formed that can be excited by the lasers. Several ways to prevent molecular collisions have been proposed, such as using optical lattices to confine the molecules [39], or inducing repulsive interactions between colliding molecules using static [40], or using microwave fields [41, 42].

3. The trapping-laser excitation loss mechanism would be suppressed completely if the molecules were confined by non-optical traps, such as a magnetic trap. This would require preparation of the molecules in a low-field seeking Zeeman state, and may require nonzero electron spin.

We note that any additional effects not taken into account here—such as an increased sticking time due to external fields or hyperfine coupling, or excitations to higher excited states—can only increase the loss. Such effects could increase trapping-laser-induced loss at lower intensities, while they do not affect the high-intensity effects could increase trapping-laser-induced loss at lower intensities, while they do not affect the high-intensity limit where complex formation is the rate-limiting step, see Fig. 4.

To summarize, we find that experimentally observed losses of nonreactive ultracold molecules cannot be attributed to sticky collisions, but they can be explained by electronic excitation of collision complexes by the trapping laser. The loss can be reduced by using significantly lower intensities and longer wavelengths. The loss can be prevented by using a magnetic instead of optical trap, repulsive box potentials, or by preventing molecular collisions. The theory is illustrated for NaK+NaK collisions.
Other bialkalis, such as NaRb and RbCs, have comparable electronic structure and longer sticking times, such that we expect trapping-laser-induced loss to also be the major cause of losses for these systems.

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