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Photoionization Spectroscopy of KAu and NaAu Diatomics

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The new metal diatomics KAu and NaAu are studied using resonant two-photon ionization (R2PI) electronic spectroscopy. These species are produced by laser vaporization of a "salted" gold rod in a pulsed nozzle cluster source. Analysis of the spectra provides the vibrational constants for the excited states and correlations to specific atomic asymptotes. Energetic cycles provide determinations of the ground-state dissociation energies. The values are $D_0'' = 2.75 \pm 0.2$ eV for KAu and $D_0'' = 2.64 \pm 0.2$ eV for NaAu. These dissociation energies for the heteronuclear diatomics are significantly greater than those for the corresponding homonuclear diatomics Na_2, K_2, or Au_2. Partial ionic character in the ground state bonding is implicated, analogous to that observed previously for silver and copper-alkali diatomics.

Introduction

Electronic spectroscopy of metal dimers has often been used to study the details of metal−metal bonding.[1−16] There are many studies of homonuclear metal dimers composed of the alkali or noble metals, including species such as Na_2, K_2, and Au_2.[1−3] Since the development of laser vaporization sources, refractory metals have become easier to study and many transition metal dimers have been investigated. Recent work has included heteronuclear diatomics that contain transition metals, such as AlCu, AlPd, AlAg, AlAu and AlNi.[1,4−8] Other recently studied mixed metal dimers include AgCu, CuAu, AgAu, TiZr, TiNb, and ZrV, although this list is far from comprehensive.[9−12] Recent experiments in our lab have focused on the electronic spectroscopy of heteronuclear dimers in which an alkali atom is combined with a main group or transition metal atom.[13−17] The main group examples include species such as LiAl and LiMg.[13,14] More recently, we have explored the series of alkali−noble metal diatomics, KAg,[15] LiCu,[16] LiAg,[16] and NaAg.[17] Theory has only just begun to examine such species.[19−22] In the present report, we extend these studies to examine for the first time gold-containing species in the form of NaAu and KAu.

Studies of heteronuclear dimers are interesting because of the role metal−metal bonding plays in catalysis and at the interfaces between microelectronic circuit components. For example, bimetallic surfaces are known to have catalytic activity that is significantly different from that of monometallic surfaces.[23] Recent research has investigated the microscopic details of metal−metal bonding at bimetallic surfaces, especially including alkali films on transition metals.[24] The corresponding diatomics provide simple model systems, tractable for theory and experiment, in which the representative features of the electronic structure and bonding in these systems can be explored.

Previous examples of mixed metal dimer spectroscopy were possible because alloy samples were available for the metal combinations of interest. However, alloys of main group or transition metals with alkali metals are not generally available and cannot be used to make mixed diatomics. Mixed metal clusters for these systems have been prepared with two separate oven or laser vaporization sources coupled in the same experiment.[25−27] To make a simpler source with a single sample, we have prepared composite samples containing two immiscible metals. In one method, a solid rod of a transition metal is coated with a vapor deposited thin film of alkali metal. It is then possible, for example, to make copper or silver rods coated with lithium which we have used in previous studies.[16] Another method, which is much simpler, involves "salting" the surface of a transition metal rod with an alkali halide by simply rubbing the powder onto the roughened rod surface. In either method, laser vaporization of the composite rod produces both metals together in the gas phase, and mixed clusters are formed. These methods of sample preparation are general, making it possible to study many mixed metal or metal compound clusters. For the gold−alkali systems in the present study, we use the salting method to produce the desired samples.

The noble metals are particularly convenient for spectroscopic studies due to the closed d-shell atomic ground-state electron configuration ($nd^{10}[n+1]s^1$).[28] The alkali atoms have the same s^1 valence configuration. The limited number of valence electrons for both of these greatly simplifies theory and spectroscopy on the resulting metal dimers due to the low density of excited molecular electronic states.[1,2] It is expected that the combination of either a Na or K atom with a Au atom will result in a simple s−s σ bond, with a $^1\Sigma^+$ ground state (0_g^+ in Hund's case c). $^1\Sigma^+$ ground states have been predicted by theory and/or measured previously for related species such as LiCu and LiAg.[16−22] Likewise, the low number of excited atomic states for these metals should produce relatively few excited molecular states. However, Au, Na, and K have several low-lying atomic states and so the density of molecular states may begin to be significant for the diatomics composed of these metals.

The opportunity also exists to compare the mixed metal dimers NaAu and KAu to their covalently bonded homonuclear counterparts Na_2, K_2, and Au_2, whose properties are well-known.[2] The homonuclear species necessarily exhibit pure covalent bonding. However, because there is a large difference in electronegativity between Au and Na or K, a significant degree of ionic character is expected in the bonding for the heteronuclear systems.[29] The bond energies determined here for

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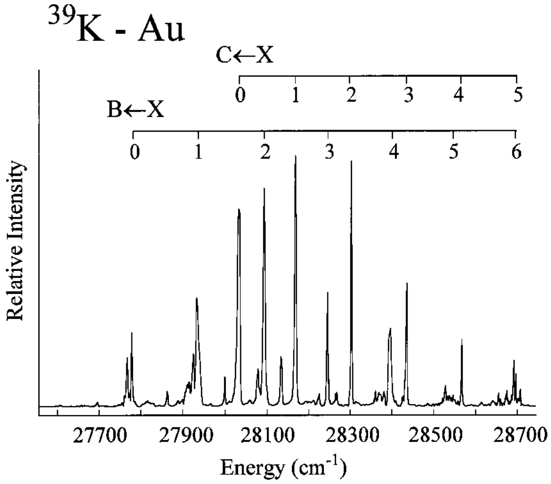

Figure 1. Resonance-enhanced 1 + 1 photoionization spectrum of ^{39}KAu in the 364−348 nm wavelength region. The progressions are assigned to two electronic band systems.

NaAu and KAu are greater than those of the corresponding homonuclear species, consistent with such ionic bonding.

Experimental Section

Samples containing both gold and sodium or potassium are produced by "salting" a gold rod with the alkali chlorides. The appropriate powder is rubbed into the surface of the rod with a plastic scrubbing pad. Laser vaporization of the salted rod produces a plasma containing both gold and alkali atoms. Vaporization is accomplished with a XeCl excimer laser (Lumonics 860) in a pulsed nozzle metal cluster source[30] with conditions adjusted to produce small molecular species. The molecular beam machine and mass spectrometer for these experiments have been described previously.[30]

After expansion, the molecular beam passes through a skimmer into a time-of-flight mass spectrometer, where resonance-enhanced two-photon photoionization (R2PI) is accomplished with a Nd:YAG (Spectra-Physics GCR-3) pumped dye laser (Lumonics HD-500). The output of the dye laser is frequency doubled using a Lumonics HypoTRAK-1000 autotuner with a BBO or KDP crystal. The visible light is blocked with a filter. Spectra are calibrated with alkali or gold atomic transitions which are measured in the same wavelength region.

Results and Discussion

KAu. Spectra were found for the KAu diatomic in three energy regions near 355, 285, and 238 nm. The spectra measured are shown in Figures 1−3. As shown, the density of vibronic levels is low near 355 nm, higher near 285 nm, and lower again near 238 nm. In all spectra, the signals are strong for 1 + 1 photoionization with one color. Gold has only one isotope with significant natural abundance (^{197}Au), but potassium has two (^{39}K, 93.3%; ^{41}K, 6.7%).[32] All of the spectra reported below are measured in both the 236 and 238 parent ion mass channels. The figures show the spectra for the more abundant ^{39}KAu isotopomer.

The ionization process here is one-color, two-photon throughout the spectra studied. We can therefore place limits on the ionization potentials (IP's) of the species detected. The highest energy resonance level is at 42857 cm^{-1}, which places a lower limit on the ionization potential for KAu of 5.31 eV. The upper limit for the IP is given by twice the energy of the lowest observed level at 27778 cm^{-1}. The IP of KAu lies therefore in the region 5.31 ≤ IP ≤ 6.88 eV.

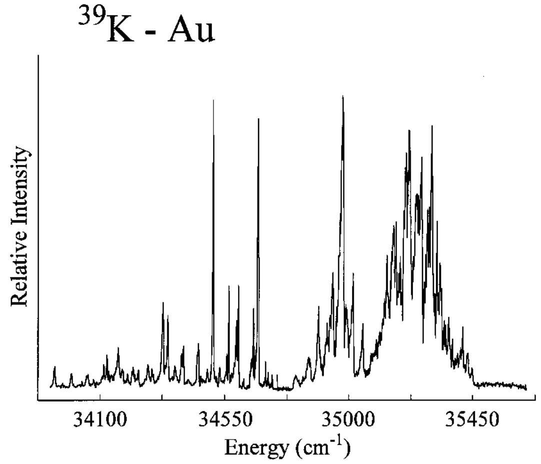

Figure 2. Spectrum of ^{39}KAu in the 294−282 nm wavelength region. The structure here is too complex to analyze.

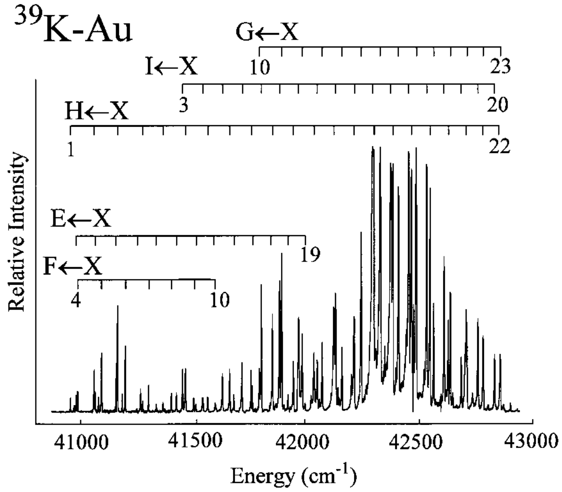

Figure 3. Spectrum of ^{39}KAu in the 244−233 nm wavelength region. Progressions in five band systems are assigned.

Figure 1 shows two progressions labeled B ← X and C ← X (see discussion below) in the region around 355 nm. Altogether, 56 vibrational bands are observed and assigned. These band positions are given in Table 1. These are assigned to two different electronic band systems. The higher intensity bands result from excitations beginning in the vibrational ground state ($v'' = 0$). The less intense ones are hot bands from the ground-state level $v'' = 1$. From these hotband positions, we determine the ground-state fundamental frequencies of $\Delta G_{1/2} = 169$ cm^{-1} for ^{39}KAu and $\Delta G_{1/2} = 168$ cm^{-1} for ^{41}KAu. The transitions are observed for the minor isotope (^{41}KAu) on all cold bands and a limited number of hot bands. The isotopic shifts then establish that the first observed vibrational band for both states is $v' = 0$. The vibrational constants determined for the B state are $\nu_{00} = 27778$ cm^{-1}, $\omega_e = 160.0$ cm^{-1}, and $\omega_e x_e = 1.0$ cm^{-1} for the ^{39}KAu isotope. Extrapolation of the excited-state progression via a standard Birge−Sponer plot leads to a dissociation energy of $D_0' = 6379$ cm^{-1}. For the C state, the values are $\nu_{00} = 28033$ cm^{-1}, $\omega_e = 137.6$ cm^{-1}, $\omega_e x_e = 0.81$ cm^{-1}, and $D_0' = 5877$ cm^{-1}. Due to the nested progressions and the presence of hotbands, several of the bands observed are blended with those from other progressions (see line positions in Table 1). However, the number of blended lines in

TABLE 1: Measured Band Positions for the Lower Energy Region of the Spectrum for KAu (cm^{-1})[a]

v', v''	B ← X	C ← X
0,0	27777.9/27777.7	28033.4/28034.1
1,0	27933.6/27928.7	28168/28165.1
2,0	28093.3/28083.2	28302.4/28298.5
3,0	28245.2/28231.3	28435.3/28426.6
4,0	28396.4/28380.3	28566.8/28555.1
5,0	28546.3/28521.1	28696/28682.7
6,0	28695.9/28659.6	
0,1		27862.9/27867.3
1,1	27767.0/27767.1	27999.5/28000.6
2,1	27924.7/27920.5	28133.3/28132.7
3,1	28078.0/28067.6	28266.5/28261.0
4,1	28229.2/28212.5	28399.3/28390.3
5,1	28380.4/28356.8	28527.4
6,1	28527.2	28655.2/28644.8
7,1	28672.9	
0,2		27696.1
2,2		27967.1
3,2		28099.5
4,2	28059.6	
5,2	28210.5	

[a] Isotopic bands are indicated as ^{39}KAu/^{41}KAu.

any progression is small, and the resulting additional uncertainty in band positions has a negligible effect on the constants determined.

Figure 2 shows the ^{39}KAu resonances near 285 nm. As shown in the figure, the spectrum in this region is very complex with many overlapping transitions and/or broad lines. No analysis of the spectrum in this region is therefore possible.

Figure 3 shows the spectrum in the higher energy region near 244−233 nm. In this region, there is also a dense pattern of bands and some overlap, but analysis is possible. All the bands with an intensity of more than 5% of the most intense band can be assigned to five different progressions, which are labeled E−I as shown. In these systems, 137 bands are assigned for the two isotopomers. These are listed in Table 2. Again, there are several blended bands from different progressions (see Table 2), but the number of such bands in any one progression is small. The spectrum shown is connected from about 10 different scans over different dye regions, and no attempt is made to correct for dye curve intensity variations. The vibrational assignments are made with isotopic shift data, although the shifts are small. The F ← X state has particularly small shifts and a more limited data set, and therefore, the vibrational assignment is more uncertain. An assignment with the upper state vibrational quantum number shifted to a value one higher than that given in Table 2 leads only to a slightly worse fit. The vibrational constants and the dissociation energies for all observed upper states are listed in Table 3. The 0−0 band is not observed for any of the progressions in this energy region. The ν_{00} values given in Table 3 are therefore all extrapolated using the vibrational constants determined. Extrapolations using a Birge−Sponer plot can also be made to determine the approximate dissociation energies for each of these excited states. These plots exhibit good linearity, indicating that the Morse potential approximation is not extremely bad. In the case of the H ← X and I ← X systems, the progressions are extensive and a large fraction of the excited state is measured. Convergence limits can be obtained by simply adding the 0−0 band energy for each state to its dissociation energy ($\nu_{00} + D_0$). These limits, which are useful in correlating the molecular transitions to atomic asymptotes as described below, are also given in the table.

The vibrational frequencies for the E, F, G, and H states are all near 110 cm^{-1}, their anharmonicities range from 0.7 to 1.0 cm^{-1} and their convergence limits are all close together at 44300 ± 600 cm^{-1}. Therefore, the potentials are similar, suggesting that they may have similar bonding orbitals in the excited state. The I state, which has transitions in the same energy region, has a quite different potential. The vibrational frequency and the anharmonicity are clearly lower ($\omega_e = 89.9$ cm^{-1}, $\omega_e x_e = 0.36$ cm^{-1}) and the convergence limit (46871 cm^{-1}) is much higher than those of the E, F, G, and H states.

If these various excited electronic states can be correlated to specific atomic asymptotes, energetic cycles can be used and estimates for the ground-state binding energy can be obtained. However, the number of excited states measured and the number of possible atomic states to which they might correspond makes this procedure problematic. The low-energy atomic asymptotes for gold and potassium atoms and their energies are Au ($5d^9 6s^2$) $^2D_{5/2}$ + K ($4s^1$) ^2S at 9161 cm^{-1}, Au ($5d^{10}6s^1$) ^2S + K

TABLE 2: Measured Band Positions in the Higher Energy Region of the Spectrum for KAu (cm^{-1})[a]

v'	E ← X	F ← X	G ← X	H ← X	I ← X
1				40954.2	
2				41057.5/41052.3	
3				41161.3/41153.1	41449.6/41443.4
4		40985.3/40973.9		41262.8/41253.3	41538.2/41530.2
5		41090.6/41078.1		41363.5	41625.0/41615.1
6		41195.0/41180.3		41461.8/41449.6	41710.9/41699.3
7	40969.3	41298.5/41281.5		41560.3/41545.2	41796.6/41782.2
8	41061.8	41399.9/41381.3		41656.1/41640.2	41876.8
9	41153.0/41136.2	41498.5		41751.7/41734.6	41961.3
10	41246.2	41593.5	41795.4	41845.9/41825.3	42044.2/42025.1
11	41336.5/41314.1		41885.8/41868.1	41937.4/41917.0	42126.2/42106.4
12	41421.7		41977.7/41955.0	42030.1/42006.0	42208.4/42185.6
13	41508.2		42067.0/42040.3	42119.2/42094.8	42288.5/42265.8
14	41593.5		42154.8/42125.7	42208.4/42182.1	42368.4/42343.6
15	41675.3/41649.8		42239.8/42209.9	42294.4	42448.6/42421.9
16	41756.9		42322.9/42292.3	42379.2/42349.2	42528.1/42499.9
17			42403.1/42371.9	42461.7/42431.2	42606.8/42577.0
18	41914.1		42481.8/42451.6	42544.2/42513.1	42684.4/42652.8
19	41991.1		42560.2/42527.6	42625.7/42593.9	42757.2/42726.5
20			42635.4/42602.4	42703.9/42672.6	42831.5/42799.9
21			42708.3	42780.8/42746.9	
22			42780.8/42746.9	42857.2/42820.1	
23			42854.2/42820.1		

[a] All transitions originate from $v'' = 0$. Isotopic band positions are indicated as ^{39}KAu/^{41}KAu.

TABLE 3: Molecular Constants of the Excited and Ground States of KAu[a]

state	ν_{00}	ω_e	$\omega_e x_e$	D_0	convergence limit
I	41185	89.9	0.36	5686	46 871
	41187	89.5	0.34	5826	
H	40846	107.9	0.71	4077	44 923
	40845	108.1	0.72	4041	
G	40768	113.0	0.93	3426	44 194
	40793	109.6	0.83	3603	
F	40538	116.7	1.01	3383	43 921
E	40266	106.8	0.80	3563	43 829
C	28033	137.6	0.81	5877	33 910
	28036	136.4	0.63	7361	
B	27778	160.0	1.00	6379	34 157
	27780				
X	0	$\Delta G_{1/2} = 169$			
	0	$\Delta G_{1/2} = 168$			

[a] The states with two lines contain entries for ^{39}KAu and ^{41}KAu, respectively. The units are cm^{-1}.

(4p^1) $^2P_{1/2,3/2}$ at 12985/13043 cm^{-1}, Au (5d^{10}6s^1) ^{2}S + K (5s^1) ^{2}S at 21027 cm^{-1}, Au (5d^{9}6s^2) $^2D_{3/2}$ + K (4s^1) ^{2}S at 21435 cm^{-1}, Au (6s^1) ^{2}S + K (3d^1) $^2D_{3/2,5/2}$ at 21534/21547 cm^{-1}; and Au (5d^{10}6s^1) ^{2}S + K (5p^1) $^2P_{1/2,3/2}$ at 24701/24720 cm^{-1}. A doubly excited state occurs for Au (5d^{9}6s^2) $^2D_{5/2}$ + K (4p^1) $^2P_{1/2,3/2}$ at 22116/22204 cm^{-1}. The density of additional atomic asymptotes increases toward higher energy, with the next group of states near 27 400 cm^{-1}. Because of the low ionization energy of potassium and the high electron affinity of gold, there is also an ion pair asymptote of the form Au$^-$ (6s^2) ^{1}S + K$^+$ (4s^0) ^{1}S at 16389 cm^{-1}. Depending on the well depth assumed for the ground state, the excited states we observe could be matched up with any number of possible asymptotes. The situation is made worse because the extrapolations we perform to obtain the convergence limits of each excited state are substantial. In all cases except the H ← X and I ← X band systems, the extrapolation is much more than half of the excited potential.

To make the assignment of these asymptotes, we assume that the strong transitions observed should correlate to asymptotic atomic resonances which are allowed. Although spin−orbit effects are large for gold and significant intensity may be found for nominally forbidden resonances, potassium states should not exhibit a strong effect in this regard. We therefore focus on singlet−singlet transitions. We also assume that the best assignment will provide a match for as many as possible of the molecular convergence limits with specific atomic resonances. We have found such an assignment which we believe is the most likely one. The lowest energy asymptote of Au (5d^{9}6s^2) $^2D_{5/2}$ + K (4s^1) ^{2}S gives rise to the molecular states $^3\Pi$, $^1\Delta$, and $^3\Delta$. These are all nominally forbidden from the $^1\Sigma^+$ ground state, and therefore we do not expect to observe strong transitions to any of these states. For the numbering system, we count the $^1\Delta$ as the A state (and the $^3\Pi$ and $^3\Delta$ states are a and b). The strongest allowed atomic transition at low energy is the ^{2}P ← ^{2}S (4p ← 4s) on potassium at 12985/13043 cm^{-1}. This occurs in a region where there are few other states. Two molecular states (Σ and Π) are expected to correlate to this asymptote. We therefore assign transitions to these as the B ← X and C ← X band systems, which occur in a region of relatively low state density, to correlate to this asymptote. This assignment in turn determines the relative positions of all the other excited molecular states. Systems E−H ← X are therefore in position to correlate to the cluster of atomic transitions in the 21000−22000 cm^{-1} region. The I ← X system was noted to have a noticeably higher asymptote than the other systems in the same wavelength region by about 3000 cm^{-1}. This is consistent with its correlation with the ^{2}P ← ^{2}S (5p ← 4s) potassium resonance at 24701/24720 cm^{-1}. The highly congested region of the spectrum near 285 nm then falls at a position where the ion pair curve could cross and perturb the intensity of other molecular states, explaining the complexity in this region. This general assignment explains all the qualitative features in the positions of the spectrum and the relative densities of states. No other assignment does this. Although it is clear that the E−H ← X systems must correlate to the atomic transitions in the 21000−22000 cm^{-1} region, specific assignments are not possible because there are too many atomic asymptotes falling in the same wavelength region within the uncertainty of the extrapolated convergence limits.

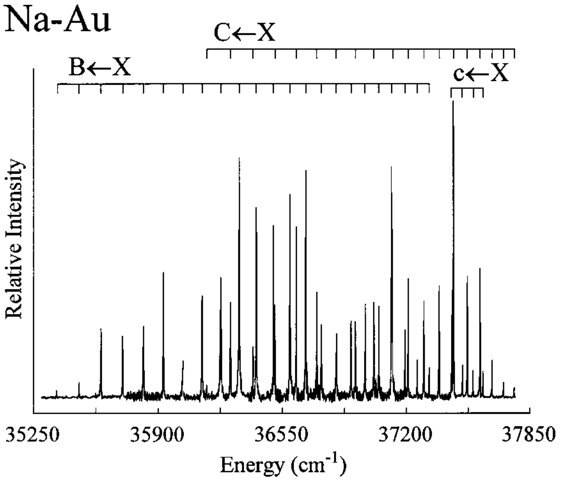

Figure 4. Spectrum of NaAu in the 282−265 nm wavelength region. Two long progressions are assigned to separate band systems, and there is a short progression in a third system.

With this assignment, we can estimate the ground-state bond energy for the molecule. To do this, we focus on the B/C ← X and I ← X systems, where distinct assignments are possible. The convergence limits for these states obtained by extrapolation then give the ground-state bond energy directly by subtraction of the corresponding atomic asymptote energy. Thus, the B ← X and C ← X systems should converge to the same atomic K ^{2}P ← ^{2}S (4p ← 4s) limit. We take the difference between the average of the ^{39}KAu convergence limits (34033 cm^{-1}) and the average of the atomic spin−orbit multiplet (13014 cm^{-1}) to get a ground-state bond energy of 21019 cm^{-1} (2.61 eV). The same procedure using the I ← X limit and the K ^{2}P ← ^{2}S (5p ← 4s) resonance, yields a ground-state bond energy of 22160 cm^{-1}(2.75 eV). Of these two procedures, the extrapolation of the I ← X system is likely to produce much better energetics because the measured levels cover a larger portion of the excited potential and the extrapolation is much shorter. Various assignments of the E−H excited states to atomic transitions in the 21000 cm^{-1} region likewise produces bond energies in the 2.6−2.9 eV energy range. We therefore report a conservative value for the dissociation limit for KAu of $D_0'' = 2.75 \pm 0.2$ eV.

NaAu. Spectra for NaAu were only found in one wavelength region near 275 nm (35300−37800 cm^{-1}). The spectrum recorded is shown in Figure 4. Two long progressions and a short one are observed. There is no clear evidence for hot bands and we assign the progressions as derived from the ground-state $v'' = 0$. The spectrum shown was derived from experiments with five different samples on 2 days. Both gold and sodium have only one isotope (^{197}Au, 100%; ^{23}Na, 100%), and therefore, we can measure the spectrum only in the 220 mass channel. It is therefore not possible to measure isotopic shifts for the bands observed, and we cannot determine the quantum numbering for

TABLE 4: Vibronic Bands Observed for NaAu

n'	B ← X	C ← X	c ← X
0	35371.7	36153.8	
1	35488.6	36277.5	
2	35602.6	36395.3	
3	35714	36510.5	
4	35821.4	36621.7	
5	35927.4	36729.6	37438.6
6	36029.6	36833	37495.2
7	36129.2	36932.6	37550.3
8	36227.4	37028.1	37603.8
9	36322.5	37120.6	
10	36412.6	37208.5	
11	36502.2	37291.6	
12	36589.5	37371.4	
13	36673.9	37448.2	
14	36755	37520.2	
15	36833.9	37587.6	
16	36910.4	37652	
17	36984.5	37711.9	
18	37056.1	37768.4	
19	37124.7		
20	37192.1		
21	37256.2		
22	37318.8		

TABLE 5: Molecular Constants of NaAu in cm^{-1} Units

state	ν_{00}	c_e	$\omega_e x_e$	D_0	convergence limit
c	≤37439	58.4	0.78	≥1092	38531
C	≤36154	126.9	1.96	≥2055	38209
B	≤35372	122.4	1.30	≥2885	38257
X	0				

these bands. As before, we can place limits on the ionization potential of NaAu from the 1 + 1 photoionization band positions. The highest energy resonance level in this case is at 37319 cm^{-1}, which places a lower limit on the ionization potential for NaAu of 4.63 eV. The upper limit for the IP is given by 2 times the energy of the lowest observed line at 35371 cm^{-1}. The IP of NaAu lies therefore in the region 4.63 ≤ IP ≤ 8.77 eV.

The intensities on the low-energy end of both of the progressions observed vanish gradually in the noise, and therefore, we strongly suspect that we are not observing the origin band transitions. We therefore use an arbitrary counter n' to label the bands, where $n' \leq v'$. The bands observed are listed in Table 4. We can fit these bands to a vibrational energy equation of standard form $E(v) = c_e(v + 1/2) - \omega_e x_e(v + 1/2)^2$, where c_e is a fitting parameter and $c_e \leq \omega_e$. As indicated, the anharmonicity thus determined does not depend on the quantum numbers. The vibrational parameters determined this way are shown in Table 5.

We can extrapolate these progressions to their convergence limits, as discussed above for the KAu spectra. Although a normal Birge–Sponer extrapolation requires a specific knowledge of vibrational quantum numbers, we use a corresponding linear extrapolation of vibrational interval versus energy to determine the convergence limit. The energy at the calculated limit ($D_0' + \nu_{00}$) does not depend on the unknown vibrational numbering. The value derived for the B ← X system is 38257 cm^{-1} and that for the C ← X system is 38209 cm^{-1}. If these limits can be identified with specific atomic state asymptotes, then subtraction of the atomic resonance energy yields the ground state bond energy for the molecule. The low-lying atomic states for sodium and gold are well-known. The only low-lying excited limits are Au (5d^{9}6s^2) $^2D_{5/2}$ + Na (3s^1) ^2S at 9161 cm^{-1}, Au (5d^{10}6s^1) ^2S + Na (3p^1) $^2P_{1/2,3/2}$ at 16956/16973 cm^{-1}, Au (5d^{9}6s^2) $^2D_{3/2}$ + Na (3s^1) ^2S at 21435 cm^{-1}, and Au (5d^{10}6s^1) ^2S + Na (4s^1) ^2S at 25740 cm^{-1}. A doubly excited asymptote of Au (5d^{9}6s^2) $^2D_{5/2}$ + Na (3p^1) $^2P_{1/2,3/2}$ lies at 26117/26134 cm^{-1}. The transitions detected are strong in intensity, and therefore, we believe they most likely correlate to an allowed atomic resonance. We therefore assign the asymptotic state to be Au (5d^{10}6s^1) ^2S + Na (3p^1) $^2P_{1/2,3/2}$. Two molecular singlet states (Σ and Π) are expected to be derived from these atomic states, and we count these states as B and C, as explained above for KAu. We use the average of the spin–orbit multiplet energy (16965 cm^{-1}) and the average of the energies for the convergence limits (38233 cm^{-1}) to derive a ground-state well depth of $D_0'' = 21268$ cm^{-1} (2.64 eV). From an estimate in the errors in the extrapolation procedure, we assign an uncertainty of ±0.2 eV. A series of four bands with weak intensity are also observed in this region near 37400–37600 cm^{-1}. Since no additional singlet states are expected here, we tentatively assign these bands to the singlet–triplet c ← X system.

The ground-state binding energies determined here for the mixed complexes NaAu (2.64 eV) and KAu (2.75 eV) are larger than the values for the homonuclear diatomics Na_2 (0.72 eV), K_2 (0.514 eV), and Au_2 (2.29 eV). This suggests that there is a significant ionic contribution to the bonding in the mixed complexes. As discussed by Pauling,[29] the percent ionic character of a heteronuclear diatomic with a single bond can be estimated by

$$\% = 1 - \exp[-(c_a - c_b)^2/4]$$

where the c values are the electronegativities for the respective atoms. With the values for the electronegativities for Na (0.93), K (0.82), and Au (2.54),[31] the ionic character of NaAu is estimated to be about 48% and that for KAu is estimated to be about 52%. A strong M^+,Au^- ionic contribution is therefore expected for the ground-state bonding, consistent with the bonding behavior reported previously for other alkali/noble metal diatomics.[13–17] Ionic bonding is reasonable for these systems because of the low ionization potentials of sodium (5.14 eV) and potassium (4.34 eV) and the high electron affinity of gold (2.31 eV). The resulting difference IP(Na) − EA(Au) is 2.83 eV and IP(K) − EA(Au) = 2.03 eV. These are the energy separations between the ion pair asymptote, $M^+ + Au^-$, and neutral ground-state atoms, M + Au.

We have previously studied the related diatomics LiCu, LiAg, NaAg, and KAg,[13–17] which also exhibit ionic bonding behavior. Morse and co-workers have studied LiCu in different wavelength regions.[18] In each case, the bond energies for the mixed metal diatomics are estimated to be significantly greater than the corresponding homonuclear diatomics because of ionic character. Gold has a higher value for the electronegativity than either copper or silver, and consequently, the ionic character in the present diatomics is particularly high. Consistent with this, the bond energies seen here are also greater than those for other alkali–noble metal mixed diatomics, e.g., D_0(LiCu) = 1.95 eV, D_0(LiAg) =1.89 eV,[16] D_0(NaAg) = 1.59 eV.[17] If we consider the lowest IP alkali metal (Cs) taken together with the most electronegative noble metal (Au), an especially high ionic character would be expected for CsAu, which would then be another interesting diatomic system to study. In the case of the lighter molecules (LiCu, LiAg),[16,18] rotationally resolved spectroscopy led to the determination of bond lengths for these species. The bond lengths in these heteronuclear diatomics are shorter than the values for the homonuclear systems, consistent with the stronger bonding. Rotational resolution is beyond our present capability for the gold diatomics with sodium and potassium, but a study of LiAu may be interesting in this regard.

The bond energies and ground-state vibrational frequencies determined here now provide some of the first information available for gold−alkali diatomics. Theoretical investigations are numerous for alkali metal dimers, and theory is able to provide good agreement with experiment for these systems. However, gold presents special challenges for theory in the large number of electrons, large spin−orbit interaction, and the importance of relativistic effects. The data provided here may provide good targets for theoretical investigations of these effects.

Conclusions

The new NaAu and KAu diatomics are investigated using laser vaporization and resonant two-photon ionization spectroscopy. Seven excited states of KAu and three of NaAu are measured. The density of electronic states observed for these gold−alkali diatomics is much higher than that seen previously for corresponding silver and copper systems, which makes analysis more difficult. However, in regions where analysis is possible, the vibronic level structure is investigated, and values for the binding energies of these molecules are estimated. The data are compared to the previously reported molecules LiCu, LiAg, NaAg, and KAg. Ionic bonding character is demonstrated by high dissociation energies for the heteronuclear diatomics relative to their homonuclear counterparts. The specific bond energies and vibrational frequencies obtained here for these first examples of gold−alkali diatomics may provide targets for theoretical investigations of metal bonding in heavy atom systems.

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